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THE

PHYSICAL REVIEW.

PHYSICAL PHOTOMETRY WITH A THERMOPILE ARTIFICIAL EYE.

By Herbert E. Ives and E. F. Kingsbury.

THE idea of a physical photometer, an instrument to indicate luminous intensities by the position of a pointer, is comparatively old.[1] The feasibility of the idea has been demonstrated, notably by Fery,[2] but it has not heretofore found application in practical form. That this is the case is chiefly because the great field (although not the only one) for the physical photomoter is in the photometry of lights of different color, and this latter is a problem only recently given a satisfactory solution.[3] Put differently, we may say that the physical photometer has had to lie dormant because there has been no way to determine definitely whether a given physical photometer reads correctly.

The present paper describes the development and practical use of an artificial eye, consisting of a sensitive thermopile in conjunction with an absorbing medium whose transmission is a copy of the spectral luminosity curve of the average eye. This artificial eye differs from previous essays in the same direction in the accuracy with which it conforms to the latest determinations of the luminosity curve and in the fact that it has been exhaustively tested for its performance upon test color differences whose photometric values have been established by a satisfactory method of colored light photometry.

Necessary Photometric and Physical Preliminaries.

As a preliminary to the detailed description of the new physical photometer it is desirable to summarize the state of development to which the solution of certain photometric and physical problems must have been brought before physical photometry could be put in practical form.

The Adoption of a Method of Visual Colored Light Photometry.—We may emphasize two features which are practically indispensable in a method

of visual colored light photometry if it is to serve as a basis for physical photometry. First, the method must conform to the elementary arithmetical axioms that things equal to the same thing are equal to each other, and that the sum of the separately measured parts shall equal the measurement of the whole. The importance of this is best illustrated by an example of a photometric method which is quite unsuitable, namely, "visual acuity." By this method a monochromatic light measures as more effective than a polychromatic one of the same or greater intensity, as measured by other criteria. Obviously any attempt to develop a physical photometer which shall discriminate between monochromatic and other radiation of the same intensity is beset with extreme difficulty. Second, the visual photometric method should be used only at one definite point in the "condition diagram" determined by brightness and field size. In other words, the infinite number of values which are theoretically possible owing to the existence of the Purkinje and allied phenomena, must be reduced to a single one by the adoption of definite standard conditions of illumination and field size. The practical importance of this restriction lies in the obvious difficulty of constructing a radiometer which shall change its relative spectral sensibility with the intensity of total illumination and with the size of the object presented to its view. This latter restriction is not a serious one although it might at first sight so appear. It is not serious because the study of the photometric problem has shown the disturbing phenomena mentioned to be of importance only at very low illuminations. The adoption of standard high illumination conditions is as necessary to visual colored light photometry as to physical. Deviations from these standard, most useful conditions, are to be met by the use where necessary of correcting "quality factors."

The method of visual colored light photometry to which we have worked in this research is that specified by the use of the flicker photometer, with a photometric field of 2 degrees diameter, under an illumination to give the brightness of a white surface under 25 meter candles, a large enough group of observers being used to form an average eye.

The Establishment by the Visual Photometric Method of a Set of Luminosity Values of Representative Color Differences.—The most important and useful color scale is of course that given by the luminosity curve of the normal equal energy spectrum. With this accurately determined by a photometric method conforming to the arithmetical axioms, the physical photometer problem consists solely in the accurate copying of the curve by the spectral sensibility curve of the radiometer. If the different parts of the spectrum measure correctly then all mixtures of these parts must measure rightly.

The luminosity curve of the equal energy spectrum has been determined by substantially the photometric method outlined by Ives and by Nutting.[4] The curves obtained are shown in Fig. 1 (dashed and dot-and-dashed lines). They are in general similar, but differ somewhat in area and shape of the blue side. These differences will show up as small but detectable differences in the relative values of the complex colors and, pending still more exact determinations of the luminosity curve, the choice of the exact curve to which the physical photometer must conform must be made by a process of trial on other color differences.

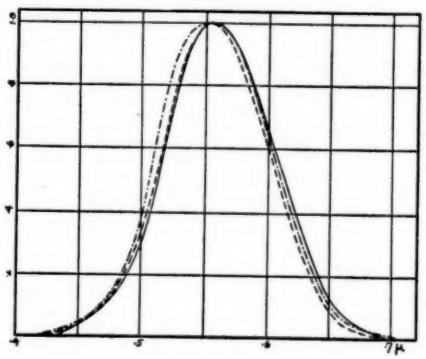


Fig. 1.

Luminosity curves of the equal energy spectrum. Dot and dash line, Ives' data. Dashed line, Nutting's data. Full line, Curve called for to secure agreement between visual and physical photometer values on series of test colors (transmission curve of final luminosity curve solution).

It may be remarked in reference to the spectrum luminosity curve that while its exact determination is all that is necessary to provide a color scale, the practical experimental difficulties, due to the necessity of determining the intensity of the radiant energy through the visible spectrum, are great enough to leave the results so far obtained in some doubt where the greatest accuracy is in question.

The spectral luminosity curve must, therefore, be supplemented by other test colors, whose luminosity values are capable of more exact determination. Such colors are suitable for checking the performance of a luminosity curve solution and for indicating slight changes, but are not suitable for determining it originally. We have had at our disposal for this purpose a series of absorbing solutions, developed for other purposes, whose transmissions have been determined by the standard photometric method by a group of observers representing the average of 61 individuals. These solutions have been described in detail elsewhere. It is only necessary to list them here. They consist of four, as follows:

1. A solution of potassium dichromate in water,
72 grams to one liter solution.
2. A solution of cupric sulphate in water,
53 grams to one liter solution.

These two solutions, placed in one centimeter thick matched glass tanks, should transmit equal amounts of the light from a standard "4-watt" carbon lamp, as determined by the standard visual photometric method. These solutions we have developed[5] and used for the selection of groups of observers whose mean visual characteristics shall be the same as our large group of 61. We shall refer to them here as the "test colors."

3. A yellow solution which in varying concentrations reduces the light from an incandescent solid to visual equivalence with that from incandescent solids at lower temperatures.

Composition.

Cobalt ammonium sulphate	100	g.
Potassium dichromate	.733	g.
Nitric acid (1.05 grav.)	10	c.c.

Mix with distilled water to one liter of solution.

4. A blue solution which in varying concentrations reduces the light from an incandescent solid to visual equivalence with that from incandescent solids at higher temperatures.

Composition.

Nickel ammonium sulphate	50	g.
Ammonia (.90 grav.)	50	c.c.
Ammonium sulphate	10	g.

Mix with distilled water to one liter of solution. Dilute with distilled water containing 10 g. ammonium sulphate per liter.

These solutions[6] we shall refer to as "Fabry solutions," the possibility of the development of such media having been pointed out by Fabry.[7] The transmission of these solutions in thicknesses of one centimeter, at 20° C., against clear water, are accurately given by the equations:

Yellow solution over "4-watt" lamp	$\log_{10} T = -.245\, c^{.9}$
Yellow solution over tungsten lamp to reduce to "4-watt" color	$\log_{10} T = .368\, c^{1.05}$
Blue solution over "4-watt" lamp	$\log_{10} T = -.539\, c^{1.03}$

where "c" (concentration) is expressed in decimal fractions.

The spectral transmissions of these solutions are shown in Fig. 2. It will be seen that solutions 1 and 2 give a comparatively sharp division of the spectrum (of the carbon lamp) into two complementary parts, while the Fabry solutions give a very gradual change of intensity from end to

end. We have as well in the yellow solution on the test lamp side, and in the blue solution on the carbon or comparison lamp, side, two means of obtaining the same visual color difference, with slight differences in the spectra.

These solutions give us, therefore, two main different types of color difference, and include the most common type now encountered, namely that between the low and high efficiency incandescent lamps. We have worked upon the assumption that a physical photometer which conforms

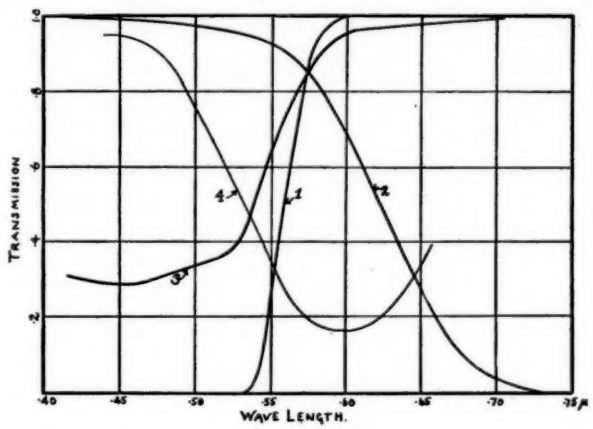


Fig. 2.

Spectral transmissions of colored solutions used to test performance of physical photometer. 1. Yellow test color. 2. Green test color. 3. Fabry yellow solution, 35 per cent. conc. 4. Fabry blue solution, 100 per cent. conc.

closely to the determinations of the spectrum luminosity curve and as well measures these color differences accurately is sufficiently practical for immediate needs.

The Existence of a Satisfactory, Highly Sensitive Means of Measuring Radiant Energy.—Luminous flux being simply radiant power which has been passed through an evaluating medium, either the retina or a luminosity curve solution, the physical measurement is necessarily one of radiant power measurement. An essential characteristic of the radiometer to be employed is of course that it shall have adequate sensibility to stand the tremendous reduction of intensity which transformation from radiant power to luminous flux involves with our present light sources (a reduction usually of about 99 per cent.). In addition to this the radiometer should give a response directly proportional to the stimulus. Further, its spectral sensibility should be fixed and unchangeable in order that the problem of altering its sensibility to that of the eye shall be capable of definite solution.

In the preliminary study of the problem of physical photometry[1] the chief types of radiometer were studied with reference to the essential characteristics for this purpose. The most sensitive ones (selenium and the photo-electric cell) were found to be deficient in certain essentials and final choice was made of the thermopile, which has of late been subject to considerable study and development.

PRACTICAL DETAILS.

The Thermopile and Galvanometer.—The thermopile used in the majority of the work was a linear one of bismuth-silver, Coblentz design, of 18 junctions, having a total resistance of 26 ohms, the junctions being in series. The galvanometer was a d'Arsonval, constructed by Leeds & Northrup. Its period was 6.5 seconds; its internal resistance 12.5 ohms; its critical damping resistance 32.5 ohms and its sensibility 33 mm. per microvolt.

The Luminosity Curve Solution.—The luminosity curve solution was worked out by trial with the spectrophotometer, to conform quite closely to the luminosity curve as determined by Ives. At the same time the number and character of the constituents was such that by altering their relative proportions the transmission curve could be altered to correspond quite closely to the characteristics of the Nutting curve, or toward the characteristics of individual curves in the groups of which the ones quoted are average. This first approximation to the working solution was composed as follows:

Cupric chloride	60 grams.
Cobalt ammonium sulphate	7.5 grams.

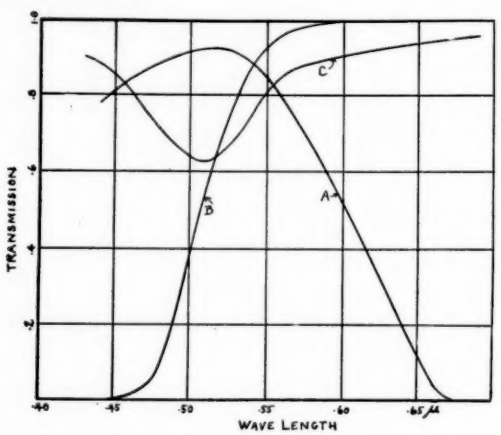


Fig. 3.

Spectral transmissions of constituents of luminosity curve solution. *A*. Cupric chloride. *B*. Potassium chromate. *C*. Cobalt ammonium sulphate.

Potassium chromate	1.7 grams.
Nitrid acid (1.05 gr.)	15 c.c.

The chromate should be dissolved separately and the acid added to it. These constituents have been carefully selected for permanence and other practical qualities.

In Fig. 3 are shown the transmission of the constituents separately. This solution has a transmission closely that of the Ives curve and it will be easily seen that it should be possible by altering the amount of the cobalt constituent to remove the chief difference between that and the other experimental luminosity curve obtained by Nutting and by changing the copper or potassium chromate to shift the curve bodily toward red or blue. The Nutting curve we find is very accurately copied by the following composition.

Cupric chloride	68 grams.
Cobalt ammonium sulphate	14 grams.
Potassium chromate	19 grams.
Nitric acid (1.05 gr.)	15 c.c.
Water to	1 liter.

The Arrangement of Apparatus and Method of Reading.—Fig. 4 shows the arrangement of apparatus to scale, as set up in our physical photom-

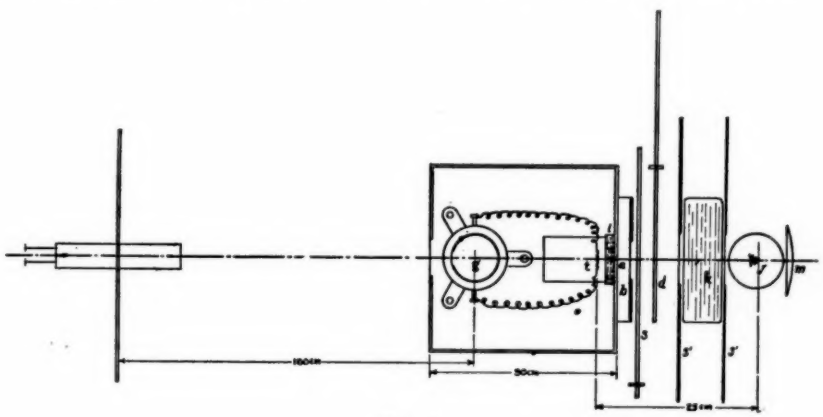


Fig. 4.

Diagram of thermopile artificial eye. *t*, thermopile; *l*, luminosity curve solution; *g*, galvanometer; *j*, lamp; *s'*, screens; *k*, protective water tank; *s*, shutter; *d*, sector disc; *b*, ledge holding absorbing media to be measured; *m*, mirror.

eter room, a basement room 10 × 10 feet square, where the temperature is reasonably constant.

The thermopile *t*, the luminosity curve solution in a one centimeter thick glass tank *l*, and the galvanometer *g*, are all placed close together on the top of a concrete pier in an enclosing box. The box has a small

aperture *a*, facing toward the 100-candle-power stereopticon lamp *j*, 25 cm. distant. The radiation from the latter passes through openings in two tin screens s^1 and through the water tank *k*. This latter was adopted originally for the purpose of keeping the surroundings of the thermopile from unnecessary heating, and is, we find, essential but for this purpose and to completely obstruct infra-red radiation. A shutter *s* and a sector disc *d* are interposed between the luminosity curve solution and the water tank. The absorbing solutions to be measured are placed on a ledge *b*. *m* is a concave mirror which may be placed behind the lamp to increase the size of the deflections when desired.

The apparatus as shown in the diagram is arranged for the measurement of absorptions. It can, however, be just as well utilized for measuring the intensities of light sources. With the point source carbon lamp, which gives approximately 45 candle power at "4-watt" color, we obtain deflections of 7 centimeters without the concave reflector, or as much as 20 with it. For the measurement of absorption the sensibility may be greatly increased by the use of a convex lens between light source and thermopile. Smaller light sources could be brought considerably nearer the thermopile. Actually we find no advantage in going over five centimeters with the deflections, so that we believe the sensibility of the apparatus in its present form is sufficient for all ordinary purposes. Candle-powers as low as 8 can be measured accurately.

The chief impediments to accuracy in physical photometry we have found to be mechanical disturbance, drift and lack of exact proportionality between stimulus and response in the galvanometer. Mechanical disturbances depend for their magnitude upon the location of the laboratory and the location of the galvanometer in the laboratory. With the d'Arsonval galvanometer magnetic disturbances are not to be feared under usual conditions; purely mechanical ones are slight in the ordinary basement and, where heavy machinery is near, we find the Julius suspension very effective. In short, the arrangement we have adopted is entirely practical from this standpoint for the average laboratory.

Drift of the galvanometer-thermopile system we find by far the most serious trouble we have to contend with. Even in a room at unusually constant temperature there is apt to be a slow creep of the zero, amounting sometimes to several per cent. of the reading during the time taken for a deflection and the return to zero. We believe that much of this might be eliminated by enclosing the galvanometer and thermopile in a thermostat, as could be done easily with the whole system occupying the small space it does here. Experiments along this line are now in progress in connection with another problem. Meanwhile we have found it easy

to meet this difficulty by making the manner of reading such as to automatically eliminate the effect of drift. To do this we make our readings on a timed basis. We have found with our system that by allowing exactly the same time interval between the first zero reading, the deflection and the final zero reading, that the true zero may be taken as the mean of the first and last readings. We find 30 seconds a convenient and sufficient period of exposure. In addition to this procedure we so arrange that all our deflections are of approximately the same size, securing this condition by the use of the sector discs (operated by a distant motor to avoid magnetic disturbances).

Any lack of exact proportionality between stimulus and deflection such as is caused by an off-center suspension of the galvanometer coil, is also neutralized by the use of the sector disc to maintain the deflections of the same size. Another source of error, which falls under the same head, is a slow change in the sensibility of the system, which we notice at times. The exact cause of this we have not determined. It may lie in the gradual heating up of the entire thermopile, or it may lie entirely in the galvanometer. We find that this effect may usually be reduced by exposing the thermopile steadily for some minutes before beginning regular work. It is, however, our practice, in addition, to alternate the readings on the standard and test lights so that any effect on the result is eliminated. We have good reason to believe that most of these difficulties are to be ascribed to the very severe conditions with respect to acid atmosphere and dust peculiar to our laboratory, situated in the midst of gas works.

By following these precautions we have no difficulty in securing a precision of better than one per cent.

We may remark here parenthetically that the attainment of this degree of precision with a degree of sensibility adequate to measure the usual light sources suggests the desirability of applying this physical method to precision photometry even where there is no problem of color difference. For instance the intercomparison of standard lamps. Under good laboratory conditions a precision three or four times as good as we attain should be easily possible.

Since the greater part of the work here reported was completed we have made a trial of a vacuum thermocouple with very promising results. This, constructed by Dr. E. Karrer and in general agreement with the design of Dr. A. H. Pfund,[8] consists of a single junction (with a second similar junction for compensation) of BiSn, BiSb alloys, in a glass container exhausted with the aid of a charcoal evacuator. This junction has a very small mass, but is connected to a rather large mass of metal intended to act as a heat reservoir.

We find this junction to be more definite in action and freer from drift and changing sensibility than the exposed type. Where it is possible to make or obtain thermocouples of this type we believe they will give great satisfaction.

We mention the trial of this extra junction in order to suggest that a more systematic study of the galvanometer-thermopile system than we have made may be expected to greatly improve on the precision obtained by us.

The Changes Found Necessary in the Original Luminosity Curve Solution.—With the luminosity curve solution matching the Ives curve as described, the first set of color differences measured were those given by the yellow Fabry solution. It was found that over the range represented by the commoner illuminants and standards, namely, from the Hefner to the "1 watt per candle" tungsten, the agreement between visually determined and physically determined values was practically perfect.

Beyond this range of color difference, however, a progressive divergence appeared, greater where the blue end of the luminosity curve was in question than where the red end was most used. Thus on the "comparison lamp" side[9] the difference between visual and physical values approached one per cent., at the end of the observed curve, on the "test lamp" side, where the color difference amounted to that between a "4-watt" and a "half-watt" lamp, the difference was as much as two per cent. Now, although these differences fall well within the scattering points obtained by a group of selected observers, we considered it undesirable to stop short of exact agreement and, therefore, undertook a cut and try modification of the luminosity curve solution.

As the first step in this we measured the two "test" colors. These we found to measure two per cent. off the visual value, the yellow solution measuring too small. We had then at our disposal several means of effecting a correction. We could decrease the concentration of the cupric chloride, thereby making the system more red sensitive. Or we could increase the concentration of either the cobalt or the chromate. Bearing in mind that the chief difference between the Nutting and Ives curves lies in the blue-green, the correction decided upon was an increase in the concentration of the cobalt. Such an increase was found by trial as would make the two test colors read alike.

This new solution was then tried out on the Fabry yellow, with the result that the discrepancy at the test lamp end was found little affected. It was soon evident why this was the case. The spectral transmission of the green test color is such that a change in the concentration of the cobalt constituent is very effective on it. The color difference intro-

duced by the tungsten lamp is however relatively much less sensitive to this change than it would be to a change farther from the center of the spectrum. This gave the clue to the next change, namely, an increase in the concentration of the potassium chromate. After several trials a balance was hit which behaved equally well with all the test color differences. The final solution has the composition:

Cupric chloride	60.0 grams.
Cobalt ammonium sulphate	14.5 grams.
Potassium chromate	1.9 grams.
Nitric acid (1.05 gr.)	18.0 c.c.
Water to	1 liter.

[An essential part of the absorbing means is the protective water layer of at least 2 cm. thickness.]

The spectral transmission is shown in Fig. 1 (full line), plotted to a maximum value of unity. This curve differs from the experimentally determined ones in being shifted somewhat toward the red end of the spectrum, a point which will be discussed presently. The transmission of this solution is represented very accurately by the following equation:[9]

$$L_\lambda = A\left(\frac{R_1}{\lambda}e^{1-(R_1/\lambda)}\right)^{\alpha} + B\left(\frac{R_2}{\lambda}e^{1-(R_2/\lambda)}\right)^{\beta} + C\left(\frac{R_3}{\lambda}e^{1-(R_3/\lambda)}\right)^{\gamma}$$

where

$$A = .999, \quad R_1 = .556, \quad \alpha = 200,$$
$$B = .04, \quad R_2 = .465, \quad \beta = 400,$$
$$C = .095, \quad R_3 = .610, \quad \gamma = 1{,}000.$$

Performance.—The final physical photometer measures the two test colors equal to within one half per cent. On the Fabry solutions the agreement between visual and physical values is everywhere well within one per cent. and the calculated value drawn through the visual points lies nowhere more than one half per cent. away from the physical values. This agreement we feel justified in calling complete, and, as stated above, we believe that since these test color differences are measured correctly, all other ordinary color differences of the kind met with in practical photometry (which excludes monochromatic lights) will also be measured satisfactorily. The visual, calculated and physical values for the Fabry solutions are shown in Figs. 5 and 6. These data indicate of course the accuracy to be expected in the measurement of the various light sources which the solutions counterfeit in color.

DISCUSSION.

It is not out of place to mention that the physical photometer is extremely simple and convenient in operation. It has been so arranged

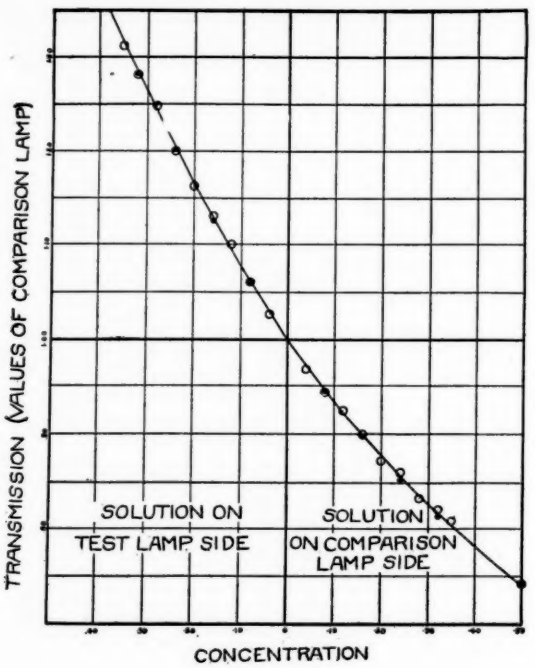


Fig. 5.

Visual and physical photometer values of Fabry yellow solution compared. Circles, visua l points; full line, calculated curve; dots, physical photometer points. The color range represented is from the Hefner, at the right, to the "half watt" tungsten, at the left.

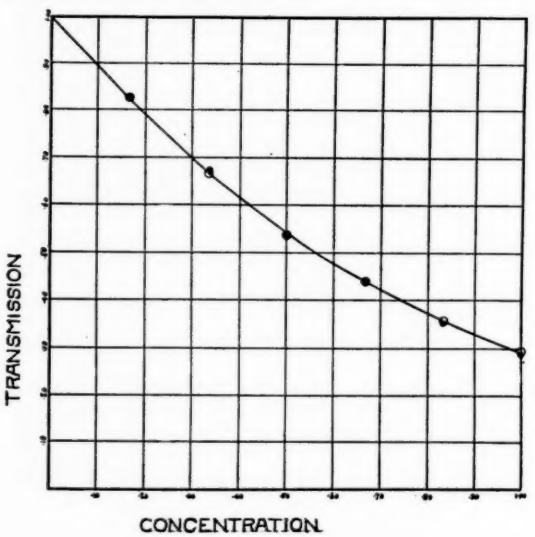


Fig. 6.

Visual and physical photometer values of Fabry blue solution compared. Circles, visua points; full line, calculated curve; dots, physical photometer points. The color range represented is from the standard carbon lamp, at the left, to the "half watt" tungsten, at the right.

that a single person can operate it perfectly. What has heretofore been a task for a group of five or more men, with a complete photometric track and accessories, can now be done by one man in a tenth the time.

The point perhaps of chief importance for discussion is the character of the luminosity curve demanded to secure the agreement between the visual and physical values. Why is it shifted toward the red end of the spectrum as compared with the directly determined ones? The explanation may lie, as already suggested, in the inherent difficulties of the direct determination. Or again it may be that our large group of observers on whom the visual values depend have a somewhat different average from the much smaller groups used in the luminosity curve determinations.

Another question of particular interest to the writers is why in our recent determination of the mechanical equivalent of light[10] the evidence was in favor of a curve shifted more toward the blue than that now indicated. The decision in favor of the bluer curve was made on the basis of the apparent better agreement, when such a curve was used, between the two methods of attack, in one of which (B) we measured the radiation transmitted by the luminosity curve solution, in the other (C) the intensity of a monochromatic green radiation.

With a view to tracing out the cause of the discrepancy which would exist were the luminosity curve as here determined employed in that investigation, we have measured on the physical photometer the transmission of the monochromatic green solution there used. We have performed the measurement both with the Nutting curve and with the new one. With the Nutting curve solution the transmission measured .0463, with the new curve .0441, the visual determined value being .0437. Now bearing in mind that the physical photometer cannot in its present form be expected to measure monochromatic light exactly right, this agreement of better than one per cent. using the new luminosity curve, shows conclusively that our visual and physical photometric work is throughout very satisfactorily consistent.

But more than that it shows that the discrepancy between the mechanical equivalent values must of necessity lie in the experimental apparatus and manipulation. No question of photometric method or of physiological or other obscure factors is at issue. Since the luminosity curve solution gives the ratio of the green light to the "white" exactly as used the new physical photometer might have been employed in the mechanical equivalent study instead of the eye and the two methods would become identical and of necessity would agree.

The answer to this riddle has fortunately been found through the accidental omission of the protective water tank in some measurements

undertaken with the physical photometer. These indicated at once what has since been verified, that there must be an infra-red transmission band in the luminosity curve solution as used in the mechanical equivalent investigation. The effect of this is to give too large a value to the energy measured by that method called (*B*).

Fortunately, as was emphasized in the account of that study, the data were obtained in such a way that they are available for any re-calculation that a change in the units or luminosity curve might later render necessary. It has therefore been possible to correct the mechanical equivalent value as the result of making one comparatively simple measurement. That measurement is of the radiant luminous efficiency of the "4-watt" carbon lamp. As previously made with the unprotected "Ives" solution (with which the actual measurements were made, and then corrected to Nutting curve values) its value was .0049. As now determined with the protective tank of water and the new luminosity curve solution, its value is .0043. This means that the value for the lumens per watt of the most efficient light, as determined with the "Ives" solution is to be increased by 12 per cent. The corrected (Ives curve) figure by method (*B*) thus becomes $563.7 \times 1.12 = 631$.

The use of the new luminosity curve also affects the value by method (*C*), since the luminous efficiency of the green mercury radiation is now reduced to 97.5. Applying this to the quantity tabulated as "*m*" in the mechanical equivalent work, we obtain the figure 630. In short, the effect of the information derived from the development of the physical photometer is to rather firmly substantiate a luminosity curve shifted somewhat toward the red as compared with the experimentally obtained ones, and to harmonize all our previous data on the mechanical equivalent of light. *As an additional result of our work we therefore announce as the corrected value of the mechanical equivalent of light*

1 lumen = .00159 watt of luminous flux.

(The new value is 2 per cent. lower than the old.)

Satisfactory as is therefore the final result of the investigation of physical photometry, it must not be overlooked that the actual luminosity curve which is worked to is only determined by the transmission of a certain inorganic salt solution. We would therefore conclude this discussion by emphasizing the importance, both from the standpoint of developing the physical photometer and for the more accurate fixing of the mechanical equivalent of light, of securing a more accurately determined luminosity curve directly, using a very large number of observers.

This is a task which could be undertaken with especial fitness by such

an organization as the Bureau of Standards. Until the luminosity curve of the spectrum is completely determined and exactly matched in the sensibility curve of a radiometer the physical photometer can be used with entire safety only for those classes of color difference for which it has been proved to agree with the visual scale. It is in fact to a certain extent empirical in its present form. Where there is any question it will be advisable to work over rather small ranges of color difference from standards calibrated by the visual method. Obviously monochromatic radiations can hardly be expected to measure correctly with any except an exact copy of the luminosity curve.

We emphasize these limitations of the physical photometer here described in order to show in which direction lies the research work which shall keep the physical photometer abreast of the probably more exacting needs of the future. As far as the present is concerned the emphasis is to be placed on the fact that we have here in practical use a physical average eye, proven capable of measuring the more usual color differences met with in practical photometry, with the same results as are given by the method of visual colored light photometry used by us.

SUMMARY.

1. A practical physical photometer has been developed suitable for colored light photometry in the standardizing laboratory.

2. A spectral luminosity curve has been determined slightly different from one previously published.

3. A corrected value is obtained for the mechanical equivalent of light.

PHYSICAL LABORATORY,
THE UNITED GAS IMPROVEMENT COMPANY, PHILADELPHIA,
April 20, 1915.

[1] See Ives, Physical Photometry, Trans. Illuminating Engineering Society, No. 1, 1915, p. 101.

[2] Fery, Journal de Physique, August, 1908.

[3] Ives, Photometry of Lights of Different Color, Phil. Mag., July, September, November, December, 1912.

[4] Nutting, Visibility of Radiation, Trans. I. E. S., No. 7, 1914, p. 633.

[5] Ives and Kingsbury, On the Choice of a Group of Observers for Heterochromatic Measurements, Trans. I. E. S., 1915.

[6] Ives and Kingsbury, Experiments on Colored Absorbing Solutions for use in Heterochromatic Photometry, Trans. I. E. S., No. 1914.

Ives and Kingsbury, Additional Experiments on Colored Absorbing Solutions for use in Heterochromatic Photometry, Trans. I. E. S., 1915.

[7] Fabry, A Practical Solution of the Problem of Heterochromatic Photometry, Trans. I. E. S., June, 1913, p. 302.

[8] Pfund, PHYS. REV., XXXIV., No. 3, p. 228.

[9] The derivation of this equation will be treated in a separate paper.

[10] Ives, Coblentz and Kingsbury, The Mechanical Equivalent of Light, PHYS. REV., April, 1915, p. 269.

A PRECISION ARTIFICIAL EYE.

BY HERBERT E. IVES.

The most attractive solution of all problems of measurement which depend upon the characteristics of a normal or average eye is to embody these characteristics in some entirely physical instrument. Among these problems may be mentioned as most important the measurement of luminosities of lights of different color, and the measurement of color. In each of these cases the value obtained by a single observer, by whatever method employed, is apt to be of little value. Numerous observers must be called upon in order to secure an average value. If, however, the properties of the average eye can be reproduced in an artificial physical eye this troublesome and often impracticable procedure may be avoided.

In a recent paper[1] a thermopile artificial eye was described, consisting of a sensitive thermopile over which is placed an absorbing solution whose transmission copies quite closely the spectral luminosity curve of the average eye. One objection which might be raised to this instrument where absolute precision is in question, is that the "luminosity curve solution" must necessarily be merely an approximation to the experimentally determined luminosity curves, and therefore not applicable to all kinds of colors. Furthermore, if it is desired to copy more than one curve, as would be the case if color measurement on the three-color basis were attempted, the labor of working out the numerous absorbing solutions may be expected to be well nigh prohibitive.

The present paper describes a thermopile artificial eye that is not open to these objections. It is a precision instrument in the sense that any wave-length sensibility curve may be exactly copied. Once the instrument is constructed the labor of copying additional curves of any type is comparatively trivial.

The apparatus is a modification of the "Apparatus for the Spectroscopic Synthesis of Color," described some time ago.[2] It consists essentially of a spectrometer forming a spectrum which is passed through a template and then recombined upon a sensitive thermojunction. By means of templates of various shapes the radiation may be evaluated in any desired way, as luminous flux, as red, green, or blue sensation, etc. The possibil-

ity of doing this was discussed by Strache,[3] in his proposal to establish the standard of light radiometrically, but to the best of my knowledge has never been tried experimentally, probably owing to the lack of sufficiently sensitive means for the measurement of the small amounts of radiant power involved.

Fig. 1 exhibits diagrammatically the complete apparatus. The image of a filament or extended light source L is formed on the slit S by means of a lens. A spectrum of this is formed by the prism P at S^1. Over this spectrum is a template, which may be in the form of a rotating disc, or which may be a flat stationary plate, as will be discussed presently. Close

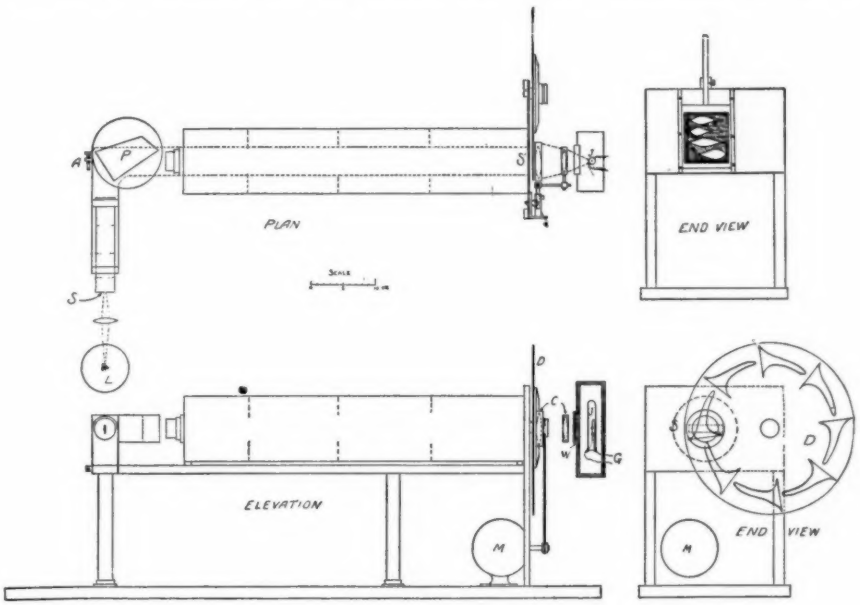


Fig. 1.

Diagram of the precision artificial eye. L, light source; S, slit; P, prism; S', spectrum; D, disc template; C, condensing lenses; W, tank for absorbing solution; J, thermopile; G, galvanometer lead; M, (clock or hand) motor; A, adjusting screw for prism table.

to the template is a lens or lens system, whose function is to recombine the spectrum, forming an image of the prism face in the color of the recombined light upon the thermojunction J. Further details of the apparatus will be described in the discussion of their functions. Detailed information on the method of calculating the openings of the templates, etc., is to be found in the paper previously referred to.[2]

By far the most important point to be determined in connection with the development of such an instrument is whether adequate sensibility can be obtained. The degree of sensibility required is very high. The

radiation to be measured lies of course entirely in the visible portions of the spectrum, a region of very low emission in all the artificial light sources which would be the subject of measurement. Moreover the intrinsic brilliancy, which is a definite limit to the amount of energy which may be received through a dispersing apparatus, is with many light sources quite low. These points are illustrated by noting that radiometric studies of the visible spectrum have been few, chiefly confined to light sources of high intrinsic brilliancy like the Nernst glower or incandescent electric lamps. These have intrinsic brilliancies of the order of magnitude of 100 or more candle power per square centimeter, while the glass mercury arc or the Welsbach mantle (in the study of which this instrument is to find its immediate use) drop below 5 of the same units.[4]

A detailed study of the factors conditioning sensibility brings out several points of interest. For a light source of given intrinsic brilliancy it is obvious that the amount of energy focused on the thermojunction is directly proportional to the width of slit employed (it being understood that the entire slit width is filled with the image of the light source). It is also directly proportional to the angular extent of the telescope lens as viewed from the point of formation of the spectrum. It is directly proportional to the vertical height of the spectrum utilizable. It is of course dependent also upon the number of reflecting and absorbing media used in the prism and lens system.

Assuming that the spectrometer system has been so designed that a spectrum is formed (of sufficient length to be practically handled by a mechanically cut template), using the maximum width of slit permitted by the purity necessary, of maximum feasible telescope aperture, as conditioned by the necessary degree of definition; utilizing the greatest vertical length of spectrum, as conditioned by the curvature of the slit image and the length of the slit image which is of uniform brightness; and possessing the minimum number of light obstructing surfaces,—the rest of the problem is that of attainable radiometric sensibility.

Probably the most sensitive means for measuring radiation, suitable for the present problem, is furnished by the thermopile with appropriate galvanometer. Using this combination the problem of sensibility consists of two parts, the thermopile problem and the galvanometer problem.

The thermopile problem is of particular interest, for this reason; that with the optical arrangement assumed the attainable sensibility is limited practically to the intrinsic sensibility of a single junction. This is made clear by considering first the recombined spectrum as entirely received upon a single junction. Suppose now it is desired to use n junc-

tions; the image of the prism face would have to be n times larger, each junction would receive $1/n$ times as much radiation; in other words the thermoelectromotive force developed would be the same. If the resistance of the n junctions is the same as that of one junction the current developed will be the same in the two cases. The only possible gain in the use of many junctions therefore lies apparently in the decreased resistance which might be obtained by joining the junctions in parallel. The resistance of a single junction is however so low in comparison with that of the galvanometer that no great gain in sensibility may be expected by the use of multiple junction piles.

This limited condition naturally directs attention to means for securing the maximum intrinsic sensitiveness of a thermojunction. In the present case use is made of a BiSn-BiSb thermojunction of the evacuated type, constructed by Dr. E. Karrer in general conformity with the design published by Dr. A. H. Pfund.[5] This junction, of alloys having a higher thermoelectric power than any pure metals commonly used, is increased in sensibility five to six times by the process of exhausting the containing vessel. It is equivalent to ten or twelve bismuth-silver junctions. The actual junction used has for receiver a tin plate approximately two millimeters square. The image of the prism face, formed by a system of three achromatic lenses, is of closely the same area, but being round projects a little beyond the junction at each side. Obvious improvements would be to furnish the junction with a round receiving plate, to secure the equivalent lens system with fewer glass surfaces, and if possible reduce the size of the prism image, since the sensibility of a junction only increases with the square root of the area. With all these changes made however it is doubtful whether the sensibility could be more than doubled; hence the use of the vacuum junction gives at least five times the sensibility to be expected from any other form now available. This factor, in the apparatus constructed, just makes the difference between adequate and inadequate sensibility.

The galvanometer employed is an iron-clad Thomson instrument designed by Coblentz. Its resistance is 5.1 ohms. Its sensibility as ordinarily used by us is from 2 to 5×10^{-10}. amperes per mm. deflection, with a period of three to six seconds. The galvanometer is enclosed in a series of soft iron pipe shields, to protect from magnetic disturbances (with which we are not however much troubled in our laboratory), and is carried on a Julius suspension to protect it from mechanical vibration. This latter is a very serious problem with us, as a 20-inch gas main direct from the near-by gas pumping station makes a right angle turn only thirty feet from the laboratory. Every throb of the pump was reflected

in a centimeter jerk of the galvanometer when this was mounted merely upon a heavy pier. The Julius suspension, constructed closely in accordance with the original publication of Julius,[6] entirely eliminated this trouble. The control magnets are mounted partly on the suspension (which is locked to a surrounding ring when these are being adjusted) and partly on the top of the shielding system. The latter magnets are used almost solely for turning the mirror to bring it in the proper part of the scale. The whole system—galvanometer, shields, etc.,—is mounted inside an enclosing box which prevents air drafts from starting long period swinging. These details are mentioned in order to show that the apparatus, although possessing high sensibility, is not impractical in form for the average laboratory, where conditions should be much better than in our own.

The first template tried was in the rotating disc form, shown in the figure at *D*. This was cut to the visual luminosity curve as recently fixed upon by work reported in this journal,[1] correcting for the absorption of the prism, shown in Fig. 2. Using a carbon lamp as the light

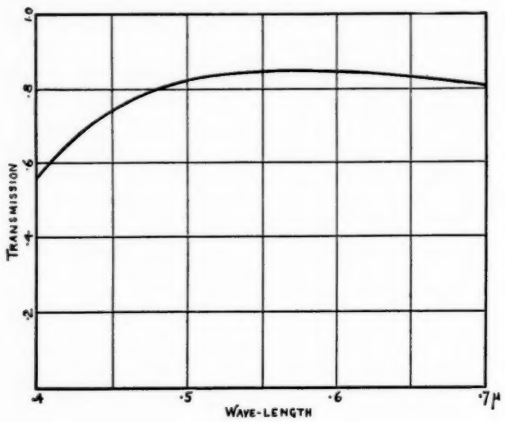


Fig. 2.

Spectral transmission of prism used in precision artificial eye. (Measurements made on block of identical glass supplied by makers of prism. Thickness 9 cm.—that of light path through prism—refractive index 1.6181.)

source, and a slit width of about 50 A.U. in the green, deflections of five or six centimeters were obtained, demonstrating the feasibility of the scheme.

It had been anticipated, however, that one of the practical difficulties would be the presence of scattered radiation, due to the hundred-fold greater amount of invisible than visible radiation. It was thought to eliminate this in part by the use of a water tank *W* before the thermojunc-

tion, but it was soon suspected that some still remained. A test experiment verified this suspicion. A solution of iodine in carbon disulfid was prepared of such concentration that only the deep red and violet were transmitted. The red and violet ends of the spectrum formed at S^1 were covered with opaque screens, and the light exposed. A deflection of about ten per cent. that previously found was now obtained. This amount of scattered radiation in spite of the presence of the water tank, and the great length of the spectrometer system, appears to the writer to cast considerable doubt on the accuracy of data on the visible end of spectral energy distribution curves obtained without the use of most elaborate means for eliminating such errors.[7]

To remove the disturbing infra-red radiation recourse was made to a screen of copper chloride, in place of the water at W. A three per cent. solution of one centimeter thickness was found best suited to meet all requirements. When using this screen of course the template transmissions must all be increased by the reciprocal of the transmission of the copper chloride. This involves the exact determination of this transmission by the spectrophotometer, whereby an undesirable but apparently unavoidable element of uncertainty is introduced. The necessity for uniform temperature also enters owing to the temperature coefficient of transmission of the copper chloride. It is possible that a copper glass would serve in place of the solution and be free from the last objection, which however is not at present serious.

As the labor of cutting the disc template is considerable it was decided to make the new curve in a fixed form. This is possible in the present arrangement where it was not in the original synthetic color apparatus[2] because in the latter the eye was used at the observing slit, and the aperture of the eye imposed an impractical limitation to the possible slit length. Where it is possible to cast upon the slit S a long uniform image, such as that from an incandescent lamp filament, the use of a fixed template is much the simplest scheme. It is only necessary to be sure that the whole width of the spectrum used receives light from the whole of the prism face, which may be tested by moving the eye up and down the vertical length of the spectrum. An advantage of the fixed template is that no motor is necessary. The latter, by the way, must in working near a sensitive galvanometer, be clock or hand driven.

To cut the new templates a photographic method was employed. The curves desired were calculated and then laid out on a large scale with drawing instruments. The parts desired opaque were painted black, and the reference wave-length line (.5461) clearly marked at the ends of the sheet. This was photographed down to the correct size and the

negative, which was made thin, was painted in the exposed parts with opaque pigment. From this a thin print on glass was made which was in turn painted with opaque paint by carefully following the edges of the exposed portions. By taking such precautions as printing in a printing frame with a black velvet back, and not carrying the development far it is possible in this way to secure beautifully clear and (with ordinary draftman's skill in the painting) accurate templates. Fig. 3 shows the

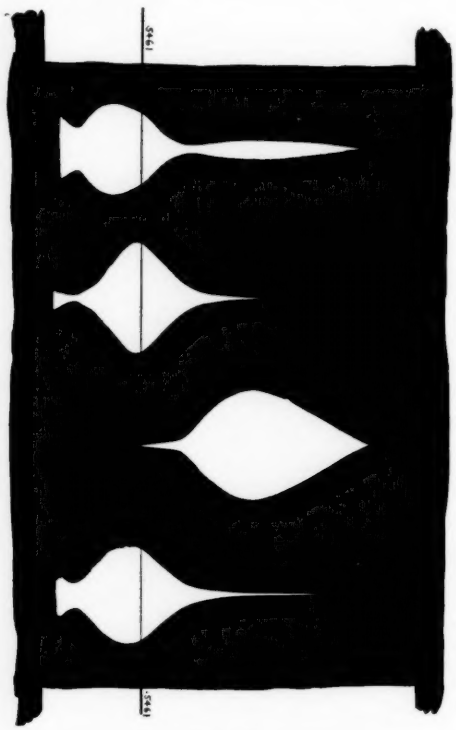


Fig. 3.

Drawing for stationary template. Top, luminosity curve. In order, blue, green and red sensation curves.

template so constructed. It has upon it the luminosity curve of the spectrum, and the red, green and blue Koenig sensation curves. The peculiar spreading at the red end is called for to offset the absorption of the copper chloride.

This glass template was mounted with adjustable clamps upon a brass frame sliding in accurate tracks, as shown in the figure (the upper "end view"). Tests of this arrangement showed entire absence of scattered radiation. It was then tried out on the same test colors used in the work on the thermopile artificial eye previously described.[1] With the

standard carbon lamp it was found possible to obtain deflections of 20 centimeters and over (workable deflections were obtained with a Cooper-Hewitt mercury arc), but more satisfactory results were given by keeping the deflections down to three or four centimeters by the introduction of extra resistance in the galvanometer circuit. Measurements made on the test colors showed very satisfactory agreement with the visual values.

In addition to the measurement of relative luminosities this instrument may be used for color measurement by the three-color system. It is only necessary to have three templates each cut to represent the mixing proportions throughout the spectrum of one of the chosen primaries and measure the relative deflections through these. The logical primaries to choose are the fundamental sensations, for instance as determined by Koenig.[8] (Measurements in terms of these may be transformed into the values obtained by using other primaries or into hue, luminosity and purity values.) These curves have been reproduced in the glass template shown in the figure, the energy distribution of a black body at 5,000° abs. being taken as "white," and have been tried out for actual color measurement.

A 3.1 w.p.c. carbon lamp was measured, the values for the three sensations coming out:

$$R = 50,$$
$$G = 43,$$
$$V = 7.$$

Values which I calculated some years ago,[9] on an assumed distribution of energy for the carbon lamp were:

$$R = 51,$$
$$G = 41,$$
$$V = 8.$$

It will be seen that these values are reasonably close to each other. There is at present no criterion by which to decide that the measured values are not the correct ones. This measurement of color is intended to be merely illustrative. A table of values on artificial illuminants may later be compiled and published.

Certain refinements are suggested on this first apparatus. For instance, the possibility of scattered light affecting the results could be met by covering each template opeining with a colored glass approximating the curve desired, letting the shape of the opening merely take up the difference between the glass transmission and the true curve. Thus a thin sheet of gold ruby for the red, a sheet of "pot" green glass for the green, a piece of "signal blue," for the blue would admirably meet the

requirements. In each case of course the spectral transmissions of the glasses would have to be accurately determined.

Now as to the uses of this precision artificial eye. First its uses in photometry. Here its chief application will be in the measurement of the transmissions of colored absorbing media to be used in eliminating color differences upon the photometer. With templates cut, as has been explained, exactly to a legalized luminosity curve of the spectrum, an instrument of this type is calculated to become a standard artificial eye, suitable for the foremost standardizing laboratories.

Second, its uses in color measurement. Here its chief application will lie in the measurement of the colors of illuminants. The general loose descriptions of lights as "snow white," etc., can be superseded by exact evaluation in definitely established units, which may be made without dependence upon the visual characteristics of a chance observer, or the necessity for comparison with a concrete color standard. The colors of glasses or other transmitting media may be determined with this instrument. These may be measured over some convenient light source, such as a carbon lamp, or if desired the templates may be so cut that while actually using a source of known energy distribution quite different from white light the results are in terms of the white light transmissions. In order to do this it is only necessary to determine with accuracy the spectral energy distribution of some convenient light sources in the visible region, a task of some delicacy but nearer practicability now than formerly.

As an illustration of a technical application of the device may be suggested the inspection of colored glass such as "daylight glass." Having determined what a correct sample (as fixed by the use of this same instrument as a synthetic color producer)[2] should measure when interposed over any convenient reproducible standard light source this value could be plotted on a color triangle, and to establish a tolerance limit a circle of size to be agreed upon by the parties interested could be drawn from this point as center. The sum of the three measured values would afford a check on any admixture of black which might decrease transmission without altering the color. Or a measurement of total transmission could also be made with the luminosity template. By this means the measurement or inspection of colored glasses could be made an exact problem. (A similar scheme giving results in entirely arbitrary units could be worked out, using three color-screens of overlapping transmissions. The instrumental sensibility required for this scheme would be far less than for the precision device.)

The description of the instrument as constructed is given here chiefly

to show that such a device is actually feasible, with the instrumental means now at the disposal of the physicist. It is limited in its application to those cases where a relatively large amount of light is available, as has been indicated, but these cases are sufficiently numerous to offer a large field of usefulness. It is to be confidently hoped that the near future will disclose means for considerably increasing the sensibility, perhaps by as much as five or ten times. It is to be expected that a detailed study of the present instrument will show possibilities for considerable improvement even with present radiometers. Such improvement as increased aperture and reduction of the number of reflecting surfaces would help materially. The thermopile can undoubtedly be somewhat better calculated for its purpose, by making the receiver round, and perhaps under some conditions by a parallel connection of

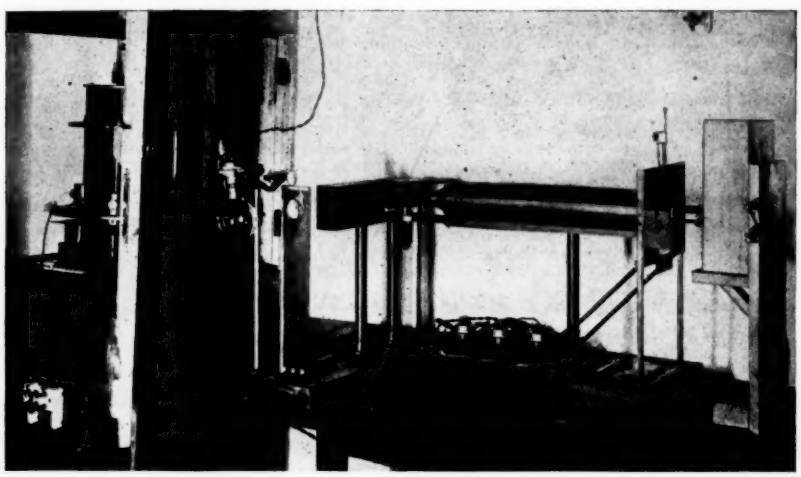


Fig. 4.

Photograph of precision artificial eye.

several junctions. There is besides the possibility that some more sensitive thermojunction will be developed (for instance bismuth-tellurium) which would be entirely satisfactory as a vacuum instrument for use with visible radiation only, restrictions which while serious in some work would not be at all so for this purpose. Could the wave-length sensibility curves of sensitized photo-electric cells[10] be controlled another form of radiometer might be utilized. Whatever may be the development of the future the writer wishes to emphasize that the first step has been taken, a precision artificial eye has been constructed and is in use.

I take pleasure in acknowledging my indebtedness to Mr. E. J. Brady,

Mr. E. F. Kingsbury and Dr. E. Karrer, who have cooperated with me at one stage or another in the development of the instrument. Special acknowledgement is also due to Mr. Charles B. Smith, whose mechanical skill and practical suggestions contributed substantially to the success of the work.

PHYSICAL LABORATORY,
THE UNITED GAS IMPROVEMENT COMPANY,
PHILADELPHIA, PA.
May 7, 1915.

[1] "Physical Photometry with a Thermopile Artificial Eye," Ives and Kingsbury, PHYS. REV., 1915.

[2] "An Apparatus for the Spectroscopic Synthesis of Color," Ives and Brady, Journal of the Franklin Institute, July, 1914, p. 89.

[3] Strache, Proc. American Gas Institute, 2, 401, 1911.

[4] "Measurements of Intrinsic Brightness by a New Method," Ives and Luckiesh, Electrical World, Feb. 16, 1911, p. 438.

[5] "A Sensitive Black-Body Vacuum Thermojunction," A. H. Pfund, PHYS. REV., XXXIV., p. 228, 1912.

[6] Julius, Annalen der Physik, 56, p. 151, 1895.

[7] R. A. Houstoun (Proc. Roy. Soc. Edin., Vol. XXXI., 4, No. 36, 1911), in agreement with this observation, found it necessary to adopt elaborate precautions to eliminate stray radiation when working in the regions of low emission.

[8] "Die Grundempfindungen," etc., A. Koenig and C. Dieterici, Zeits. für Psychologie u. Physiologie, 4, p. 241, 1892.

[9] "Color Measurements of Illuminants," Ives, Trans. Illuminating Engineering Society, April, 1910, p. 189.

[10] "Wave-length Sensibility Curves of Potassium Photoelectric Cells," Ives, Astrophysical Journal, Vol. XL., No. 2, Sept., 1914, p. 182.

THE MOBILITY OF THE POSITIVE AND NEGATIVE ION AT DIFFERENT TEMPERATURES AND AT CONSTANT GAS DENSITY.

BY HENRY A. ERIKSON.

THE object in pursuing the present investigation was to obtain evidence as to what change takes place in the size of the positive and negative ion in air when the temperature is altered, the density of the air being kept constant.

Evidence that a change takes place at temperatures less than 0° C. is offered by the results obtained by Phillips[1] and Kovarik[2] who independently determined the mobility at different temperatures. These results, however, were obtained at constant gas pressure and, therefore, do not necessarily indicate what happens when the density is kept constant, since the conditions to which the ions are subject in the two cases are not the same.

The method used was Rutherford's alternating field method as modified by Franck and Pohl. This method, from the standpoint of convenience, is well adapted for an investigation of this kind.

Fig. 1 is a diagram of the apparatus and experimental arrangement. *A* is a cylindrical vessel that has a radius of 6.2 cm. and a depth of 3.2 cm. *B* is a circular plate that has a radius of 5 cm. This plate is supported by the insulated stem *C*, and through it is connected to a quadrant electrometer. In order to reduce heat conduction a portion of the stem *C* is of glass. One centimeter above *B* is another plate *D*, of same diameter as *B*. The opening in *D* has a radius of 3.8 cm. and is covered by a brass wire gauze having nine meshes to the centimeter. The ring *D* is supported by means of three rods of quartz. A small polonium plate is attached face up at the center of the gauze. Another plate *E* is placed 4 mm. above *D*, and is supported and insulated from *D* by means of the three quartz rods.

The rays from the polonium ionizes the air between the plates *D* and *E*, which are kept at a difference of potential of about 0.8 volt by means of the battery *F*. The positive or negative ions as the case may be are

[1] Phillips, Proc. Roy. Soc. LXXVIII., 1906, p. 167.

[2] Kovarik, PHYS. REV., XXX., April, 1910.

driven towards the gauze through which some of them pass and thus become subject to the alternating field that is produced when the tuning fork alternately connects D to the positive and negative poles of the battery G. The wires connected to plates D and E pass through two quartz tubes placed one inside the other. For determining the temperature, a constantine wire is connected to the copper wire attached to E. These two wires pass without touching through the outer quartz tube.

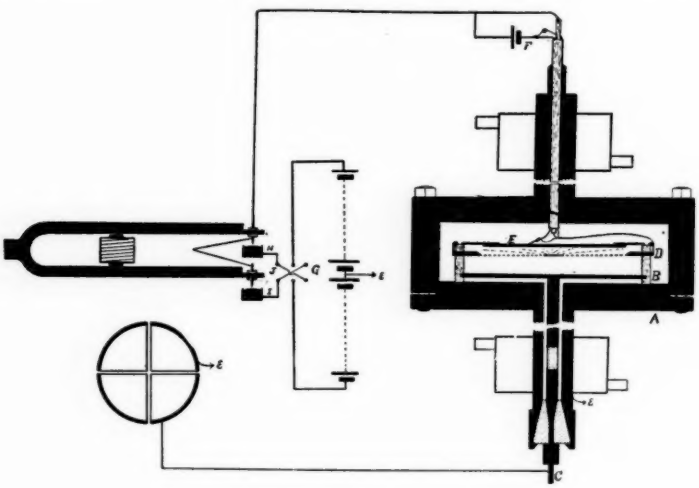


Fig. 1.

These tubes are held in place and made air tight by means of a hard wax. The ends of the upper and lower stems of the apparatus are kept at a safe temperature by means of water jackets placed as shown in figure.

This tuning fork method for shifting the polarity was found to be very satisfactory. H and I are two iron mercury cups of 8 mm. diameter. Contacts with the mercury in these cups are made through steel needles attached to the prongs of the fork. It is possible to adjust so that the mercury makes no perceptible vibration thus giving regularity of contact. Since it is difficult to secure the same interval of contact for each of the points a reversing key J was introduced and the average of an equal number of readings for each point was obtained.

By suitably adjusting the frequency of the fork and the potential of G some of the ions will reach the plate B before the field is reversed. The total charge then given to B in a given time may be measured by means of the electrometer.

This arrangement gives rise to the following relation:

$$q = it = i\left(\frac{t'}{2} - \frac{d^2nt'}{kv}\right), \qquad (1)$$

where

i = the current that flows through the gauze,

t = the time to charge the plate B to a given potential when the field between B and D is constant,

t' = the time to charge the plate B to the same potential when the field is alternating,

d = the distance between the plates,

n = the frequency of the fork,

v = the difference of potential between B and D,

k = the mobility.

In this equation d^2n/kv is the time consumed per second by the ions in passing from the gauze to the plate B.

From the above relation we see that:

$$\frac{2t}{t'} = 1 - \frac{2d^2n}{kv},$$

or

$$\frac{d}{dn}\left(\frac{2t}{t'}\right) = \frac{2d^2}{kv}, \text{ a constant.}$$

This shows that the current in the case of the alternating field which is

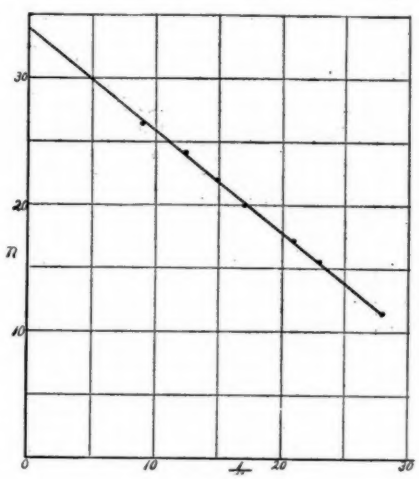


Fig. 2.

proportional to $1/t'$ is a linear function of n the frequency of alternation. That this holds is borne out by experiment the results of which are shown graphically in Fig. 2. By prolonging the line until it cuts the y axis we obtain the value of n, the frequency, for which t' becomes infinite. In terms of this frequency

$$k = \frac{2d^2n}{V}.$$

The above method necessitates the changing of the frequency of the fork. As this, in the case of the fork used, was not convenient, the mobility was calculated by means of the equation

$$k = \frac{2nd^2t'}{V(t' - 2t)},$$

which is obtained by solving for k in equation (1). Since d, n and v are kept the same they may be determined once for all, and therefore only t and t' remain to be determined at the different temperatures. It was found necessary to determine t at each temperature because it does not remain constant as the temperature is changed. This change is undoubtedly due to a greater diffusion of the ions to the gauze as the temperature is raised. The value of t is greater for the negative ions than for the positive. This is what should be expected in view of the greater diffusion of the negative ions. Another effect is noticed in the case of t. As the voltage applied from the battery F is increased from zero, the current at first increases and then diminishes. The reason for this decrease of the current through the gauze is undoubtedly due to the greater number of ions drawn to the gauze at the higher voltage values. By measuring t at each temperature the method becomes independent of these changes. There are, however, several possible sources of error that must be considered. When the temperature is altered convection currents arise. Care was taken to have the vessel well surrounded by the heating or cooling medium. The metal wall of the vessel is 1.3 cm. thick, which also aids in securing uniformity of temperature. Furthermore since the field employed, 120 volts to the cm., was such as give the ions a velocity of over 100 cm. per second the convection currents present in this case can have but a small effect. Tests made under conditions most favorable for these currents seemed to show no effect. The effect of diffusion to the sides owing to the nearness of the plates is negligible.

An uncertainty enters in connection with the conditions at the gauze at the different temperatures. During the application of the reverse field the ions are driven back giving rise to a greater ionic density near the gauze which when the direct field comes on may result in a greater current through the gauze than the steady current measured by t. Also since the diffusion is different at the different temperatures the ions may not have the same starting point under all conditions. Furthermore, there is an uncertainty in connection with the potential gradient at the

gauze and plate *B*. How important these considerations are is difficult to say. The method seems to give good values as compared with other methods. In the table below are given the results, in the order obtained, for the mobility of the positive and negative ions over a temperature range from − 21° C. to 63° C. The air involved in this set was dryed by passing through a tower of $CaCl_2$ and then through a specially designed drying tube immersed in liquid air. Before leaving this tube the air passed through glass wool. The chamber before filling was left evacuated for twelve hours and was also evacuated several times during filling with the dry air. The vessel, however, was not heated during the process of filling.

The pressure of the air was 73.5 cm. at 24.5° C.

TABLE I.

+

−184	−21	0	24	33	45	63
			1.375	1.340	1.318	1.193
			1.366	1.305	1.307	1.213
			1.334	1.333	1.208	1.216
		1.327	1.327			
		1.359				
		1.368				
		1.392	1.366			
	1.321		1.379			
	1.321					
	1.322		1.404			
1.20	1.321	1.361	1.364	1.326	1.278	1.207

−

−184	−21	0	24	33	45	63
			1.833	1.801	1.807	1.721
			1.794	1.768	1.827	1.790
			1.750	1.763	1.795	1.677
		1.602	1.707			
		1.503				
		1.495				
		1.490	1.666			
	1.638		1.576			
	1.543					
	1.607		1.524			
1.24	1.596	1.522	1.693	1.777	1.809	1.729

In Fig. 3 the average values are shown graphically by curves *A* and *B*. It is seen that the positive mobility is a maximum between the room

temperatures and zero degrees. The different values are quite regular and may be repeated with fair agreement.

The negative values, however, are quite erratic. It is seen that the ratio k_-/k_+ is normal at room temperature just after filling with the dry air. As the temperature was raised the value of the mobility diminished. When the vessel had cooled to room temperature it was found that the mobility was less than the value obtained at room temperature before heating and the same effect repeated itself after each successive heating. Apparently vapor is liberated from the apparatus during

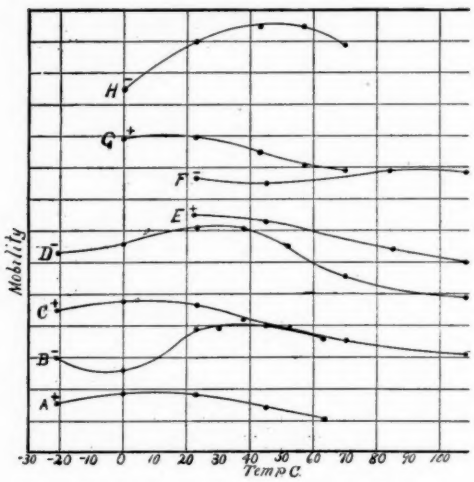


Fig. 3.

heating that reduces the mobility. Upon cooling to zero there is a large decrease in the mobility. Upon further cooling the mobility is greater than at zero indicating a dryer state due to deposit of moisture on walls of vessel.

After the above readings were obtained the vessel was evacuated and kept at a temperature well over 100 C. for an hour or more. It was then evacuated filled several times while hot with air dried by passing through $CaCl_2$ and the tube immersed in liquid air. In Table II. are given the results obtained with this sample of air. The results are arranged in the order obtained beginning in each case with the value at 24° C.

These results are shown graphically in Fig. 3 by means of the curves *C* and *D*. In this case the variation of the mobility of the positive ion is quite similar to that of the preceding case except that the diminution is somewhat greater at the higher temperatures. In the case of the negative ion there is a less sudden decrease from room temperature to

TABLE II.

+

−21	0	24	38	52	70
		1.361	1.206	1.142	1.096
	1.365	1.330			
		1.322	1.212	1.206	
		1.331			1.107
1.30		1.327	1.209	1.178	1.101

−

−21	0	24	38°	52	70
		1.882	1.84	1.687	1.534
	1.755	1.825			
		1.812	1.78	1.716	
		1.685			1.487
1.663		1.740	1.81	1.701	1.510

zero but a greater decrease at the higher temperatures. The vessel was then evacuated and filled with air that had been allowed to bubble through water before entering the chamber. The results obtained are given in the Table III.

TABLE III.

+				−			
24	45	84	110	24	45	84	110
1.321				1.560			
1.326		1.12		1.592		1.625	
1.330	1.295		1.042	1.547	1.543		1.600

These results are shown graphically by means of curves *E* and *F* in Fig. 3.

It is seen that the variation of the positive mobility is in this case about the same as in the case of the drier air used in the two preceding cases. The negative shows a maximum at a higher temperature but on the whole does not vary greatly over the temperature range employed. On account of deposit of moisture on the insulation no values for zero degrees or lower were obtained.

The vessel was now evacuated and heated to about 100° C. and kept at this temperature for a period of about five hours. During this period the pump was operating constantly. A very small stream of air from a tower of $CaCl_2$ was allowed to pass through the vessel during this time. Finally the vessel was evacuated while hot, filled several times with air passed slowly through the tube immersed in liquid air.

In the Table IV. are given the results obtained in this case.

TABLE IV.

+				−			
24	43	57	70	24	43	57	70
1.398	1.287	1.206		2.032	2.094	2.080	
1.366			1.167	1.846			1.959

These results are shown graphically by means of curves *G* and *H* in Fig. 3. It is seen that the variation of the positive mobility is about the same as obtained in the preceding cases. The negative shows a marked variation and has a maximum at a higher temperature than before.

DISCUSSION OF RESULTS.

In seeking an explanation for the variation of the mobility of the positive ion the question of clustering immediately presents itself. Since, however, the mobility of the positive ion is quite independent of the presence of moisture and also since the variation with temperature is also quite independent of the condition of the air, an explanation based on clustering seems difficult. It is possible that something is driven from the wall of the vessel during heating for which the positive ion has a special attraction. It thereby becomes loaded and moves more slowly. It hardly seems probable, however, that it would unload again as the temperature is lowered; moreover this would not explain the decrease that takes place below the temperature for which the mobility is a maximum. Definite conclusion on this point will have to be postponed until a more rigid investigation has been made. The variation of the mobility of the negative ion seems to show the effect of clustering due to moisture combined with a variation similar to that observed in the case of the positive ion. Not sufficient data has been obtained, however, upon which to base any conclusion.

In connection with the observed variations an indication based on theory is of interest. Some time ago Wellish[1] suggested that the apparently large volume of the ions is due to the effect of the charge upon the mean free path, and showed that the polarization of the adjacent molecules due to the ionic charge results in an apparent increase in the radius of the sphere of action. A little later Sutherland[2] by taking into account cohesion and electrical attraction evolved the following expression for

[1] Wellish, Phil. Trans., A, Vol. 209, p. 249, January, 1909.

[2] Sutherland, Phil. Mag., 6–18, September, 1909.

the mobility of an ion moving in a gas under the action of an electric field.

$$k = \frac{e\dfrac{dE}{dx}}{\frac{4}{3}N_3(a_1+a_3)^2\left(\frac{2\pi}{3}\frac{m_1m_3}{m_1+m_3}m_3v_3^2\right)^{\frac{1}{2}}\left\{1+\dfrac{\varphi(a_1+a_3)+\theta(a_1+a_3)}{\frac{m_3v_3^2}{2}}\right\}},$$

where

N_3 = number of molecules per cm.,[3]

$a_1 + a_3$ = the distance an ion and molecule must approach for collision,

m_1 and m_3 = mass of ion and molecule respectively,

$\varphi(a_1 + a_3)$ and $\theta(a_1 + a_3)$ are functions depending respectively upon cohesion and electric action.

By considering N_3 constant and placing

$$\frac{mv_3^2}{2} = kT,$$

where T is the absolute temperature, there results for the mobility

$$k = \frac{A\sqrt{T}}{T + C}.$$

By differentiating with respect to T and equating to zero we see that k is a maximum when $T = C$. The variation obtained, however, is greater than expressed by this equation.

SUMMARY.

The mobility of the positive and negative ions in air at atmospheric density has been measured at different temperatures by means of an alternating field method.

It was found that under the above stated conditions the mobility of the positive ion is a maximum at about 0° C. The mobility of the negative ion also shows a maximum but is more erratic in its behavior. No definite conclusion has been reached but it seems that the variation of the positive mobility is not due to clustering. The variation of the negative mobility, however, seems to be due to clustering combined with an effect similar to that causing the variation of the positive mobility.

In connection with this investigation I wish to express my thanks to Professor John Zeleny and Professor A. F. Kovarik.

PHYSICAL LABORATORY,
UNIVERSITY OF MINNESOTA,
May, 1915.

A LENS REFRACTOMETER.

BY H. F. DAWES.

THE following is a description of a convenient type of refractometer for liquids which depends on the fact that the power of a lens surface is a function of the refractive index of the substance in optical contact with it.

The principle of the arrangement is illustrated in Fig. 1. L is a double convex lens silvered on the surface A. M is a plane-parallel glass plate which touches L at B. A drop of the liquid whose index is to be found is placed between L and M. P is an object point so adjusted that the light which traverses the system to the silvered surface returns to form an image coincident with the original object. The position of P depends on the index of the liquid and may be used to find this index; the relation between the two may be found in the following way:

Fig. 1.

Notation.—Index of lens substance, n; unknown index, x; distance from B to P for adjustment described, p; radii of curvature of surfaces A, B; r, s.

The optical power of the refracting system is $(x-n)/s$. The distance, p', from B to the image of P formed by this refracting system is given by

$$\frac{n}{p'} - \frac{1}{p} = \frac{x-n}{s}.$$

Since the light must be incident normally on the surface A in order that it may be reflected as required, this image distance must equal the radius of curvature of A.

Hence $$\frac{n}{r} - \frac{1}{p} = \frac{x-n}{s}, \text{ or, } x = n\left(1 + \frac{s}{r}\right) - \frac{s}{p}.$$

In working out this relation the thicknesses of lens and plate, which

are small quantities, are neglected. The more exact formula which takes these into account is

$$x = n\left(1 + \frac{s}{r-t}\right) - \frac{s}{p-t' + \frac{t'}{n'}}$$

(t is thickness of lens, t' is thickness and n' index of plate).

The relation is thus of the form $x = c_1 - c_2/(p - c_3)$ where the c's are constants. This comparatively simple relation makes the arrangement particularly suitable for a calibrated instrument with a scale from which the index corresponding to any setting may be read off. The calibration may be done by calculation from the above formula if the optical constants are known; otherwise a number of readings may be taken with liquids of known index and a calibration curve constructed.

Details of construction.—The object of which P is the axial point consists of the cross-hair of a collimating eye-piece, or better, a small grid ruled on glass. Image and object coincide at their axial points and are equal in size (but inverted); the advantage of the grid is that the adjustment may be assisted by testing for equality of object and image as well as for coincidence by the parallax method. The cross-hair or grid will be illuminated by the monochromatic light for which the index is required, the light being concentrated on the object by means of a small condensing lens of suitable aperture.

The tube carrying the plate M telescopes into the eye-piece tube by means of a spiral screw; by this means the distance from B to P is adjusted. The calibration scale follows the screw motion. The range of values of x required in practice extends from about 1.3 to 1.75, though it is advisable to be able to set the system for x equal to 1, *i. e.*, for air in contact with the lens).

The lens slips into place in contact with M by means of a spring clip; it may be readily removed to place a drop of the liquid under test or to clean away liquid.

The whole system, must of course, be carefully centered and the surfaces optically worked.

In a typical system the following were numerical values. Index of glass, 1.544; radii of lens surfaces 41.2 cm. each. The values of p in sodium light for air, water and glycerine were; 19.71, 23.44, 25.51 cm.

Dispersion.—It is supposed that monochromatic light is used so that the calibration scale corresponds to some selected color. If the index is required for any other color the reading must be corrected for dispersion.

To determine this correction consider the light for which the indices of glass and liquid are $n + dn$ and $x + dx$. If the refractometer is

adjusted in this light the distance from P to B will be $p + dp$, given by the equation

$$x + dx = (n + dn)\left(1 + \frac{s}{r}\right) - \frac{s}{p + dp}.$$

The value of the index read off from the scale for this setting is

$$n\left(1 + \frac{s}{r}\right) - \frac{s}{p + dp}.$$

Hence the value read from the scale must be corrected by adding to it $dn\ (1 + s/r)$. Since this correction depends only on the constants of the lens it is necessary to draw up once for all a table of corrections corresponding to the different monochromatic lights available or to construct a curve showing the relation between wave-length and correction.

Sensitiveness.—The axial distance a by which object and image may be separated without showing parallax may be used to find a criterion for sensitiveness. For such a small distance of separation the correct position will lie practically midway between object and image. Hence dp the extreme error in p will be $a/2$. The corresponding error in x is dx, equal to

$$\frac{s}{p^2} \cdot dp = \frac{s}{p^2} \cdot \frac{a}{2}.$$

It appears then that the most advantageous construction is that for which p is large and s, a, small. Increase in the value of the first of these is limited, by convenience of working, to something of the order of 25 cm. so that this may be taken as a maximum value for this quantity. In considering the effect of p on the sensitiveness, it may be noted incidentally that a given instrument is more sensitive for the more highly refracting liquids since for these the values of p are larger; the calibration scale therefore becomes more open as it passes from low to high index.

The second factor, s, which enters into the sensitiveness may be diminished until the smaller aperture made necessary by the increase in curvature results in an increase in a. When the above two factors have been chosen the value of the other quantity which enters into the construction, namely, r the radius of curvature of the reflecting surface, is determined by the fundamental equation. Its value is given by substituting the selected values for p and s, the value of the index of the glass from which the lens is to be made and the maximum value of the unknown index for which the instrument is to be used.

The value of the third of the quantities affecting the sensitiveness, a, depends on the angular aperture of the pencil of light which forms the

image, on the aperture and power of the eye-piece which is used to examine the image and on the resolving power of the eye itself. Under favorable conditions a may be as small as .01 cm. With this value the above limit of error in the unknown index will be .0004 for the instrument whose dimensions are given in a previous paragraph so that the value of the index may be readily obtained to better than the third decimal place. As a matter of fact the error need not be nearly so great as the above for one may obtain a more accurate value by taking the mean of the two settings for which parallax just begins to appear (*i. e.*, image distance just too great and just too small). It will be seen that the instrument is quite as sensitive as the calibrated type of total reflection refractometer.

MCMASTER UNIVERSITY,
TORONTO, CANADA,
May 24, 1915.

A NEW FLUORESCENCE SPECTRUM OF URANYL AMMONIO-CHLORIDE.

BY EDWARD L. NICHOLS AND ERNEST MERRITT.

THE spectrum of a sample of uranyl chloride (from Kahlbaum) when excited to fluorescence at the temperature of the room was measured by the present writers in 1911.[1] Like the fluorescence spectra of other uranyl salts it was found to consist of a series of nearly equidistant bands extending from the red to the blue. The crests of the six brightest bands, according to our observations, were at .5928μ, .5631μ, .5369μ, .5121μ, .4950μ, and .4769μ. At low temperatures this spectrum, which is comparatively feeble at + 20°, is resolved into a complex of very narrow bands similar to those described,[2] in the case of the other uranyl salts, by J. Becquerel and Onnes.

In the preparation of uranyl compounds, undertaken for us in the chemical laboratory of Cornell University by Mr. G. O. Cragwell a uranyl salt was obtained in the form of tri-clinic crystalline plates which we have since found to have the composition $UO_2Cl_2 \cdot 2NH_4Cl + 2H_2O$.

These crystals are strongly fluorescent, and the fluorescence spectrum, unlike that of the other uranyl salts thus far described, is resolved at room temperature into at least eight groups of narrow bands. Each group, which corresponds to a single band of the ordinary uranyl fluorescence spectrum, consists of five nearly equidistant bands.

The symmetry of this spectrum, as it appears to the eye when viewed with a spectroscope of moderate dispersion, is most striking. While not so narrow as some of the line-like bands of uranyl spectra when excited at the temperature of liquid air, the bands are well separated from their neighbors and are about 18 Ångström units in width or one tenth as wide as the bands of the ordinary type of the uranyl fluorescence spectrum at + 20° C. Each group of five, indeed, occupies approximately the same space in the spectrum as an ordinary single band.

The distribution of intensities within the group was determined for the visually brightest group (.5302 ··· .5114), by means of the spectro-

[1] Nichols and Merritt, PHYS. REV. (1), XXXIII., p. 355.

[2] J. Becquerel and Onnes, Leiden Communications, 110, 1909.

photometer. The results are given in Table I. and are shown graphically in Fig. 1.

TABLE I.

Intensities of Bands in Group 6. (*Excited at* + 20°.)

Band.	Intensity.
.5302μ	18
.5253	33
.5203	24
.5157	11
.5114	1

[1] Visible but too dim for spectrophotometric measurement.

The curve (Fig. 1) which forms an envelope of the group of bands is of the same type as that for the distribution of intensities in a single band of the ordinary uranyl fluorescence spectrum and of the envelope of the set of bands in such a spectrum and is also similar to curves of distribution of the fluorescent spectra having a single broad band, such as resorufin.[1]

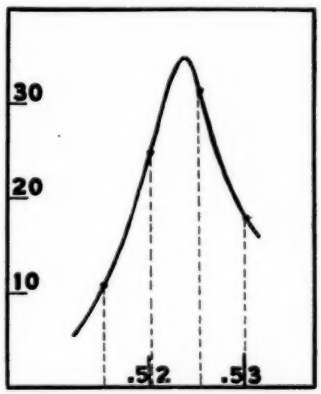


Fig. 1.

The effect of cooling is likewise analogous, the envelope for − 185° being narrower on account of the great relative reduction in brightness of the outlying members of the group. All the bands are shifted in position as well as changed in intensity in a manner to be described in a subsequent paragraph.

To determine as closely as possible the wave-lengths of the bands, photographs of the spectrum were taken. Fluorescence was excited by means of the carbon arc, the light from which passed through a screen opaque to rays of wave-length greater than about .45μ and was focused upon the crystal. Various exposures were employed on account of the great differences in the intensity of the bands and special plates were used for the red end of the spectrum. The exciting light was excluded from the camera by the use of suitable screens opaque to the blue and violet except where the absorption spectrum was to be recorded.

The various negatives were measured by mounting them on a micrometer stage in the field of the lantern. The micrometer screw was carefully calibrated so that wave-lengths could be determined by measuring the distance of the crests of the bands from certain reference lines of the mercury spectrum which was photographed on each negative so as to overlap the fluorescence spectrum.

[1] Nichols and Merritt, *l. c.*

This method of projection was found better than the use of the comparator commonly employed in the measurement of line spectra, because of the hazy character of the bands and because bands that are so weak and vague as to be invisible even under a low power microscope could be seen and located by means of the lantern. Many measurements of the stronger bands were made with comparator as a check on the determinations with the lantern.

The results of these measurements confirmed to a remarkable degree the apparent symmetry of the spectrum. When all the bands are plotted on a large scale, in a diagram with the reciprocal of wave-lengths as abscissae, the spectrum is seen to consist of eight groups of five bands each as already described. The bands of each group are very nearly equidistant, and corresponding members of the groups form an homologous series of equidistant bands. This interval moreover is very nearly the same for all five of these homologous series; but although the departures from equality are of the same order as the errors of measure-

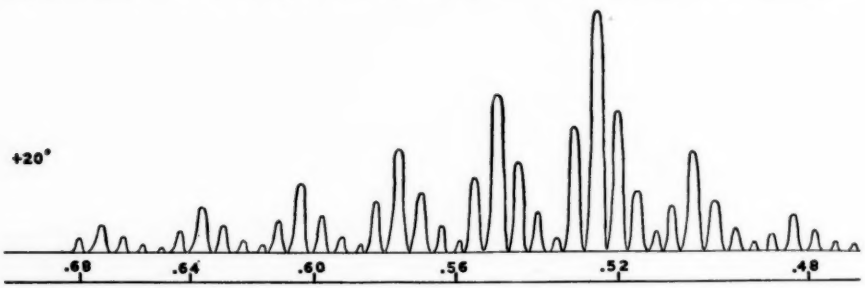


Fig. 2.

ment there is strong reason to regard them as real. Finally the groups taken as units and counting from their centers (obtained by averaging the frequencies of the bands in each) are equally distant within the errors of measurement.

The location of the various bands, as determined from the photographs, are given in Table II. The positions of the bands and their relative intensity, as estimated by the eye, are shown in Fig. 2. Horizontal distances are plotted on the scale of frequencies, the corresponding wave-lengths being indicated for convenience. In group 1, which lies in the red, band *e* is missing while in group 8 only the strongest band (*c*) was visible in any of the photographs.

This spectrum approximates very closely, *i. e.*, in most cases within or almost within the errors of observation, to a series of equidistant groups each consisting of five equidistant bands; distance being expressed in frequency. Were this strictly true the frequency interval of the

TABLE II.

Observed Positions of Bands at + 20°.

Group.	Band.	λ	$1/\lambda \times 10^3$	Group.	Band.	λ	$1/\lambda \times 10^3$
	b	.6804	1,469.7		*b*	.5547	1,802.8
	c	.6711	1,489.9		*c*	.5493	1,820.5
1	*d*	.6635	1,507.1	5	*d*	.5437	1,839.4
	e	.6585	1,521.8[1]		*e*	.5387	1,856.0
	a	.6501	1,538.2		*a*	.5344	1,871.2
	b	.6438	1,553.3		*b*	.5302	1,886.1
	c	.6356	1,573.4		*c*	.5252	1,904.0
2	*d*	.6293	1,588.9	6	*d*	.5201	1,922.6
	e	.6230	1,605.1		*e*	.5157	1,939.2
	a	.6167	1,621.5		*a*	.5114	1,955.3
	b	.6101	1,638.9		*b*	.5076	1,970.1
	c	.6039	1,655.9		*c*	.5035	1,986.2
3	*d*	.5978	1,672.8	7	*d*	.4986	2,005.7
	e	.5919	1,889.4		*e*	.4944	2,022.6
	a	.5862	1,705.9		*a*	.4906	2,038.3
	b	.5814	1,719.9		*b*	.4870	2,053.3[1]
	c	.5751	1,738.7		*c*	.4828	2,071.0
4	*d*	.5697	1,755.4	8	*d*	.4787	2,089.0[1]
	e	.5643	1,772.2		*e*	.4749	2,105.9[1]
	a	.5589	1,789.1		*a*	.4714	2,121.5[1]

homologous series of bands, *b*, *c*, *d*, *e* and *a* would be the same, and for each uniform throughout the spectrum and this interval would be the same as that between the successive groups taken as a whole. Finally the distances between neighboring bands would be the same within each group and for each group.

To test the intervals between groups the position of what may be called the center of each group was found by averaging the frequencies of all five bands and the intervals between these average positions for groups 2, 3, 4, 5, 6 and 7 were found.

Groups 1 and 8, for which insufficient data were available, were omitted.

The results are given in the tables III and IV.

The departures from uniformity in the intervals between groups (Table III.) are of the same order as the errors of observation and there is no indication of a progressive or systematic change. We may conclude therefore that within the accuracy of these measurements, *the groups are equidistant.*

[1] Band *e* (group 1) and bands *b*, *d*, *e* and *a* (group 8), which were indistinguishable in the photographs, have been assigned positions on the assumption of complete symmetry throughout the spectrum.

TABLE III.

Distance Between Groups.		
Group.	Center.	Intervals.
2	1,588.8	
3	1,671.7	82.96
4	1,754.6	82.86
5	1,837.8	83.20
6	1,921.2	83.40
7	2,003.9	82.76

TABLE IV.

Distance Between Neighboring Bands (Average).		
Band.	Center of Series.	Intervals.
b	1,762.1	
c	1,779.9	17.86
d	1,797.6	17.73
e	1,814.1	16.49
a	1,830.1	16.01

In a similar manner averages were found for the frequencies of each of the sets of homologous bands (*b*, *c*, *d*, *e*, *a*), and these form a group of averages, not coinciding with any actual group in the spectrum, the distances between the bands of which should however represent the mean distances of neighboring bands more closely than do the actual distances in any single group taken separately.

These averages are given in Table IV. from which it appears that the bands are not distributed uniformly within the group but that the distance between them *diminishes progressively as we pass towards the violet.* The distance between the last band (*a*) of any group and the first (*b*) of the next group is so nearly equal to the distances between the bands within the group that it was difficult, before the completion of these computations, to decide as to the boundaries between the groups. The casual appearance of the spectrum as may be seen from Fig. 2 is that of a succession of equidistant bands varying periodically in intensity. It was at first thought that the crest band (*c*) of each group formed the center with two weaker bands on either side and band (*a*) was supposed to be the first in each group counting from red towards violet. This designation has not been altered although it was found by measurement that band *a* in each group was distinctly nearer to band *b* (average distance 14.4) than to band *e* and should be considered as the last band of the group.

THE DETAILED STUDY OF THE INTERVALS OF THE SEVERAL HOMOLOGOUS SERIES OF BANDS (*b*, *c*, *d*, *e*, *a*).

To compare the intervals between homologous bands these were averaged for each series separately by the method of subtracting the frequency of each band of the series from the member of greater frequency and dividing the sum by the total number of intervals. The averages thus computed are as follows:

TABLE V.

Average Intervals between Homologous Bands.

Series.	Interval.
b (7 members)	83.19
c (8 members)	82.80
d (7 members)	83.25
e (6 members)	83.42
a (7 members)	83.26
General average,	83.20

For homologous series *b*, *d*, *e* and *a* the average distance between bands is the same within the errors of observation and approximately equal to the distance between the various groups considered as units. The interval for series *c* is smaller than for the other series and the difference, while scarcely larger than might be accounted for by experimental errors, appears to be a real one, appearing consistently in all the photographs taken of this spectrum and likewise in the case of spectrophotometric observations made to check the photographic determinations. To ascertain whether the groups of bands as individually measured really conformed to the description suggested in an earlier paragraph of a system of equidistant groups consisting of five homologous series of equidistant bands having a common interval, the positions of the members of a hypothetical system of this sort were computed in the following manner and the individual departures of the actual bands were determined.

It was assumed that the measurements of series *c* were slightly at fault and that the proper interval for the entire system was the average for the other four series, *i. e.*, 83.25. Using this interval the hypothetical bands were located about the "center" of each series and their positions were compared with those of the corresponding actual bands.

The results are shown in the following table in which the frequencies of the hypothetical bands are given in the columns marked "calculated," those of the actual bands in the columns marked "observed" and departures in those marked "differences."

THE EFFECT OF TEMPERATURE.

Ordinarily, when a uranyl salt is cooled to the temperature of liquid air the series of equidistant bands of its fluorescence spectrum, each of which corresponds to one of the eight groups of five narrower bands already described in the case of this form of uranyl ammonio-chloride, is resolved into a rather complex aggregation of narrow line-like bands.[1]

[1] See H. Becquerel, Comptes Rendus, 144, p. 671; also J. Becquerel and Onnes, Leiden Communications, No. 110, 1909.

TABLE VI.

Calculated and Observed Frequencies of the Various Series of Bands.

Series.	Group.	Calculated.	Observed.	Differences.	Intervals.
	1	1,470.3	1,469.8	+ .5	
	2	1,553.6	1,553.3	+ .3	83.60
	3	1,636.8	1,638.9	−2.1	85.60
b	4	1,720.1	1,719.9	+ .2	81.00
	5	1,803.3	1,802.8	+ .5	82.95
	6	1,886.6	1,886.1	+ .5	83.30
	7	1,969.8	1,970.1	− .3	83.95
	8	2,053.1			
	1	1,488.6	1,489.9	−1.3	
	2	1,571.8	1,573.4	−1.6	83.55
	3	1,655.1	1,655.9	− .8	82.45
c	4	1,738.3	1,738.7	− .4	82.85
	5	1,821.5	1,820.5	+1.0	81.80
	6	1,904.7	1,904.0	+ .7	83.50
	7	1,988.0	1,986.2	+1.8	82.25
	8	2,071.2	2,071.0	+ .2	84.85
	1	1,506.2	1,507.1	− .9	
	2	1,589.5	1,588.9	+ .6	81.80
	3	1,672.7	1,672.8	− .1	83.90
d	4	1,756.0	1,755.4	+ .6	82.65
	5	1,839.2	1,839.4	− .2	84.00
	6	1,922.5	1,922.6	− .1	83.15
	7	2,005.7	2,005.7	0	83.15
	8	2,089.0			
	1	1,522.7			
	2	1,605.9	1,605.1	+ .8	
	3	1,689.2	1,689.4	− .2	84.10
e	4	1,772.4	1,772.2	+ .2	82.85
	5	1,855.7	1,856.0	− .3	83.75
	6	1,938.9	1,939.2	− .3	83.20
	7	2,022.2	2,022.6	− .4	83.45
	8	2,105.4			
	1	1,538.7	1,538.2	+ .5	
	2	1,622.0	1,621.5	+ .5	83.25
	3	1,705.2	1,705.9	− .7	84.40
a	4	1,788.5	1,789.1	− .6	83.20
	5	1,871.7	1,871.2	+ .5	82.20
	6	1,955.0	1,955.3	− .3	84.10
	7	2,038.2	2,038.3	− .1	83.00
	8	2,121.4			

It was deemed of interest to determine the effect of temperature on a spectrum which was already at least partially resolved at + 20° and for

this purpose the ammonio-chloride under consideration in the present paper was subjected to cooling. Visual measurements of such of the bands as could be determined in this way were made at + 20°, 0°, − 30°, − 60°, − 90°, − 120°, − 150° and − 180°. Several sets of photographs of the spectrum were likewise obtained with the substance excited at − 185°.

When the substance, excited to fluorescence in the manner already described, was gradually cooled to the temperature of liquid air and as the spectrum was observed through the Hilger spectrometer the following changes were noted:

1. The bands become narrower and better defined until at the temperature of liquid air they correspond in appearance to the usual line like bands characteristic of the fluorescence spectra of the uranyl salts at low temperatures.

2. There is a shift towards the violet *amounting to more than a third of the distance between the bands.*

3. The following new bands appear: At about − 25° a very narrow band between *c* and *d* of each group; feeble at first but increasing in brightness with falling temperature. At about − 90° the *c* bands begin to appear double or in other words a new set becomes visible between *c* and *b*. At about − 150° another set of bands becomes visible between *e* and *a*.

Were the shift noted above the same for the different bands in each group and throughout all the groups, the spectrum at − 185°, at least as to the series, *b*, *c*, *d* and *e*, which are visible at both temperatures, would be located throughout by applying the mean observed shift to all the bands of the spectrum at + 20°.

The nature of the shift which these bands undergo appears to be as follows:

Each band may be regarded as an unresolved doublet, of which in general the member of longer wave-length is relatively so much the stronger that its position determines approximately the location of the crest of the composite band (see Fig. 3). The effect of cooling is to resolve this doublet into separately distinguishable bands and at the same time to cause a subsidence of the stronger and an increase of the weaker member. The member of shorter wave-length becomes dominant at low temperatures in each doublet and the arrangement of the entire spectrum therefore appears to be undisturbed but shifted towards the violet by an amount representing the width of the doublet.

Since however the doublet is now resolved by the narrowing of the components we might expect to be able to distinguish the original member

of longer wave-length unless by cooling it has disappeared altogether. The appearance of the group, if this be its real structure (*i. e.*, a set of equidistant doublets, the distance between the members of all the doublets being nearly the same) would then be as shown in the lower part of Fig. 3 ($-$ 185°).

At + 20°, b', c', d', e' and a' are entirely concealed by the overlapping

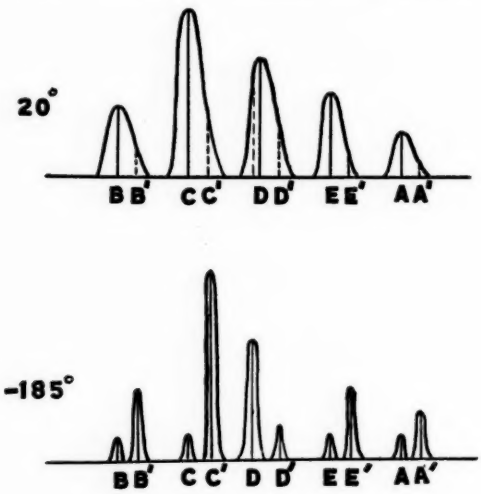


Fig. 3.

of the bands. At $-$ 185° b, c, d, e and a may or may not be visible according to their intensity or to the completeness of the resolution which in fact differs greatly in different portions of the spectrum. At $-$ 185° however b, c, d, e and a being very weak as compared with b', c', d', e' and a' or in some cases almost invisible, the appearance is that of a shift equal to the distance bb', cc', etc.

TABLE VII.

Shift of the c Series Between + 20° and − 185° C.

1/(*Observed.*)

Series.	Group.	+ 20°.	−185°.	Shift.
	1	1,489.9	1,496.5	6.6
	2	1,573.4	1,579.8	6.4
	3	1,655.9	1,662.1	6.2
c	4	1,738.7	1,744.4	5.7
	5	1,820.5	1,827.7	7.2
	6	1,904.0	1,910.6	6.6
	7	1,986.2	1,992.7	6.5
	8	2,071.6	———	———
			Average,	6.5

When we apply this test, making use of the photographic measurements at $-185°$, we find for series *c* a shift that is uniform throughout the spectrum, see Table VII.

It follows, obviously, that the interval for the *c* series is the same, within the errors of observation, at $-185°$ and at $+20°$. The actual averages from observed positions are respectively: 82.8 ($+20°$) and 82.5 ($-185°$).

For the *b* series we obtain likewise a constant shift except in the extreme red (groups 1 and 2) where the bands are so faint as to be almost indistinguishable and the resolution is imperfect so that the vague bands on the negatives are probably composite (see Table VIII.).

TABLE VIII.

Shift of the b Series Between + 20° and − 185° C.

1/(*Observed.*)

Series.	Group.	+20°.	−185°.	Shift.
	1	1,469.7	1,479.7(?)	10.0(?)
	2	1,553.3	1,563.0(?)	9.7(?)
	3	1,638.9	1,645.0	6.1
b	4	1,719.9	1,726.9	7.0
	5	1,802.8	1,810.4	7.6
	6	1,886.1	1,894.4	8.3
	7	1,970.1	1,977.9	7.8
	8	———	———	——
		Average (omitting groups 1 and 2), 7.7		

In the case of the *d* series the effect of the lack of resolution in the red end of the spectrum is more clearly marked and is capable of definite description. Here we find the bands of groups 4, 5, 6 and 7 in their expected places and showing the proper shift (see Table IX.), whereas

TABLE IX.

Shift of the d Series Between + 20° and − 185° C.

1/(*Observed.*)

Series.	Group.	+20°.	−185°.	Shift.
	1	1,507.1	1,508.9	1.8
	2	1,588.9	1,591.5	2.6
	3	1,672.8	1,675.6	2.8
d	4	1,755.4	1,761.4	6.0
	5	1,839.4	1,845.1	5.7
	6	1,922.6	1,929.2	6.6
	7	2,005.7	2,013.4	7.7
	8	———	2,097.1	——
			Average (groups 4 to 8), 6.5	

Average interval at $+20°$ = 83.24

Average interval (groups 4 to 8) at $-185°$ = 83.93

in groups 1, 2 and 3 they are considerably displaced towards the violet having a position intermediate between the places which the band *d* and the new intermediate bands should occupy. In other words in these groups of longer wave-length, these bands, which in the remainder of the spectrum are separate and well defined, are not resolved.

The interpretation of the changes occurring in the regions of the spectrum occupied by the *d*, *e* and *a* bands is most readily studied by means of the diagram in Fig. 4, in which the bands of each group at

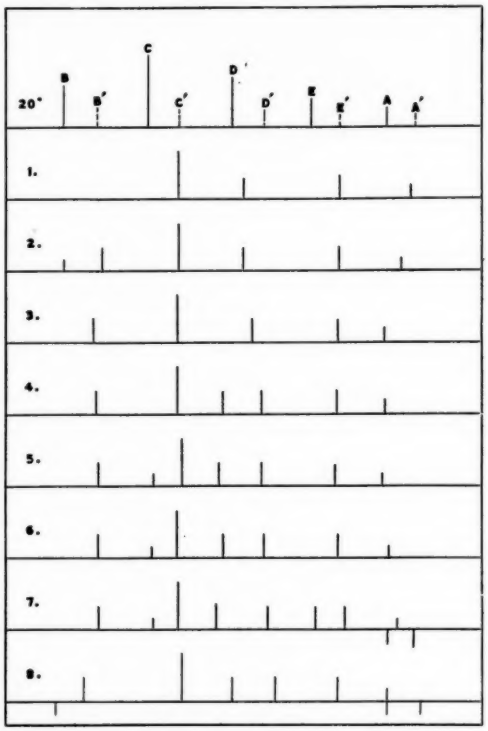


Fig. 4.

− 185° are shown in their relation to a hypothetical grouping given at the head of the column. This grouping consists of the set of imagined doublets of which as in a previous paragraph the spectrum at + 20° was supposed to be made up. The spacing for each doublet is that determined from the observed shift on cooling and the relative divergence from this arrangement is shown for all the bands of each group.

A scrutiny of the fluorescence spectrum at − 185° group by group, by means of this diagram, affords very satisfactory confirmation of this hypothesis concerning the apparent shift. It is obvious:

1. That not all the components *b*, *c*, *d*, *e* and *a* will necessarily be visible in every group of the resolved spectrum:

2. That lack of resolution in any region may give the appearance of a single band with intermediate crest in place of the doublet:

3. That the position of crests of the unresolved doublets at + 20° will not necessarily coincide exactly with that of either component.

Bearing these points in mind, it will be seen that were resolution complete all the oserved bands of the spectrum at − 185° would probably fall into the system proposed above.

We may imagine that the difference between the resolution of the bands *c* and *d*, for example as seen in Fig. 4, is produced by changes in the unresolved doublets at + 20° when the temperature is reduced to − 185°, of the kind indicated in Fig. 5. The doublet *cc'* forms a single band with crest nearly coincident with *c* at + 20° and this owing to the

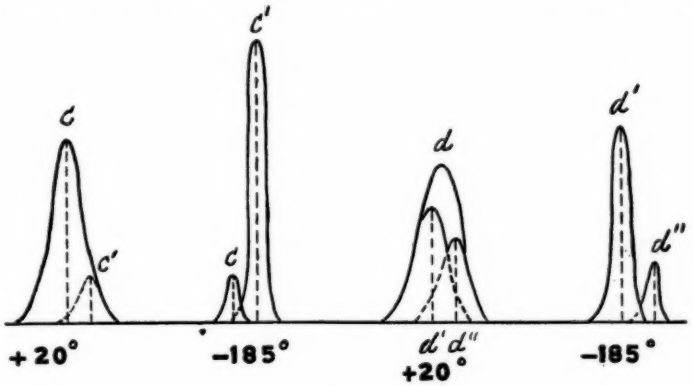


Fig. 5.

subsidence of *c* and growth of *c'* takes the resolved form shown at − 185°. In the case of *d* however the unresolved band has an intermediate crest at *d* but is really composed of overlapping components *d'* and *d''* which are separately visible at − 185°.

THE ABSORPTION SPECTRUM.

The absorption spectrum of this salt of which observations were made both visually and photographically likewise consists of several series of equidistant bands having a common interval.

Fluorescence and absorption overlap as in the case with all the uranyl spectra thus far studied, and one group of bands (group 7 of the fluorescence spectrum) which we have called the *reversing group* is common to both spectra. The bands of this group may be made to appear either as fluorescence bands or as absorption bands according to the conditions of the experiment. The reversal may be effected by the simple expedient of varying the character of the incident light. With a screen which

extinguishes the yellow and green and transmits shorter wave-lengths the fluorescence bands of this region appear on a dark background. With a yellow screen that reduces excitation to a minimum, absorption bands are seen to take their place. These, in general, coincide in position with the fluorescence they displace, but since as has been shown the bands are doublets of unequal brightness an apparent shift sometimes occurs.

The weaker band of the fluorescence pair becomes the stronger in the absorption spectrum as illustrated in Fig. 6, which is from a photograph

Fig. 6.

of such a doublet when emitting and when absorbing light. In such cases the weaker bands are often invisible unless special precautions are taken to bring them out and there is an apparent shift equal to the distance between the members of the doublet.

Since the temperature shift in the bands of the fluorescence spectrum, as stated in a previous paragraph, is mainly due to the subsidence of the stronger and the "crudescence"of the weaker member of such doublets, upon cooling to the temperature of liquid air we should expect the location of the absorption bands when thus displaced at room temperature to coincide with the low temperature positions of fluorescence, and this is found to be the case in many instances.

Unfortunately the complete analysis of the absorption spectrum is rendered difficult, not only by the varying degrees of resolution, as in the case of the fluorescence bands, but also by the existence of a general absorption which increases rapidly towards the violet and renders the crystals almost opaque to the violet and ultraviolet rays.

The absorption spectrum at $+ 20°$ extends from the reversing region into the ultraviolet.

It consists of the following series:

1. $\beta\alpha$; so designated because its first member at $.5076\mu$ ($1/\lambda \times 10^3$

= 1,970) is coincident with and a reversal of the *b* band in that group, while its second member at .4899μ ($1/\lambda \times 10^3 = 2{,}041$) is so nearly coincident with the *a* band of the same group that it may be supposed to form a close and unresolved doublet with the absorption series related to that band.

2. γ; having its first member at .5028μ ($1/\lambda \times 10^3 = 1{,}989$) and the reversal of the *c* band in that group.

3. δ' and δ; two series, having their origin on either side of the *d* band; as if this band were a doublet, unresolved in the fluorescence but resolved in portions of the absorption spectrum.

4. ϵ and ϵ'; two series, one of which ϵ begins as the reversal of the *e* band at .4942 ($1/\lambda \times 10^3 = 2{,}023$) while the companion series ϵ', which possibly belongs to an unresolved component of the *e* band, first becomes distinguishable as a faint absorption band at 2,173.

The constant frequency interval common to all these series is approximately 71[1] instead of 83.2 which is the average interval for the fluorescence bands. This sudden break to a shorter interval in passing from fluorescence to absorption is not new. It is characteristic of all absorption spectra of the uranyl salts thus far studied at room temperature[1] and corresponds, approximately, with the intervals between the absorption bands of solutions of these salts given by Jones and Strong.[2] We have tried in vain not only in the case of the chloride but likewise with the

[1] See Nichols and Merritt, PHYS. REV., Vol. 33, p. 354.

TABLE X.

Relation Between Absorption bands of UO_2Cl_2 *in Solution* (.49μ *to* .67μ) *and the* α, γ, δ *and* ϵ *Series.*

UO_2Cl_2 in H_2O Jones and Strong.		Corresponding Series of $2NH_4Cl.UO_2Cl_2+2H_2O$ (Crystals).	
λ	$1/\lambda \times 10^3$	Series.	$1/\lambda \times 10^3$ (Computed).
.6700	1,492	γ	1,492
.6500	1,538	α	1,544
.6300	1,587	δ	1,583
.6070	1,647	δ'	1,646
.6040	1,656	δ	1,653
.6020	1,661	—	——
.6000	1,667	ϵ	1,668
.5480	1,825	α	1,828
.5200	1,923	—	——
.5185	1,929	δ'	1,930
.4900	2,041	α	2,041

[1] The actual observed range, as will be seen from Table XI., is from 70.4 for series γ to 71.5 for series $\beta\alpha$, and these differences are presumably due to the varying relations of the unresolved components of the doublets of which the bands are composed.

[2] Jones and Strong, Publications of the Carnegie Institution, No. 130, p. 89, also Physikalische Zeitschrift, 10, p. 497.

crystals of the nitrate and with other solid uranyl salts, to trace the absorption into the realm of the fluorescence spectrum. Jones and Strong, however, working with solutions of uranyl chloride in water, have located various absorption bands of longer wave-lengths.

TABLE XI.

"Absorption" Bands of $UO_2Cl_2 \cdot 2NH_4Cl + 2H_2O$ *at* $+ 20°$ *C. Arranged in Series.*

Series βα.			Series γ.		
λ	$1/\lambda \times 10^3$	Average Interval.	λ	$1/\lambda \times 10^3$	Average Interval.
5,076	1,970.1		5,029	1,988.5	
4,899	2,041.2		4,860	2,057.5	
4,733	2,113.0		4,704	2,126.0	
4,577	2,185.0		——	——	
4,433	2,256.2		——	——	
4,293	2,329.5	71.5	——	——	70.4
4,166	2,400.3		——	——	
——	——		——	——	
——	——		——	——	
——	——[1]		3,815	2,620.9	
——	——[1]		3,714	2,692.8	
3,627	2 756.8		——	——	
Series δ′.			Series δ.		
4,996	2,001.6		4,978	2,008.9	
4,829	2,070.6		4,908	2,080.1	
4,667	2,142.6		4,652	2,149.5	
——	——		4,507	2,218.9	
——	——		4,370	2,288.5	
——	——	70.7	4,237	2,359.9	70.5
——	——		4,112	2,432.0	
——	——		3,997	2,501.8	
3,898	2,565.1		3,885	2,573.7	
3,792	2,637.1		——	——	
3,692	2,708.6		3,685	2,713.7	
Series ε.			Series ε′.		
4,942	2,023.3		——	——	
4,776	2,094.0		——	——	
4,618	2,165.5		4,601	2,173.5	
——	——		4,455	2,244.5	
4,331	2,309.0		4,320	2,314.6	
4,202	2,379.9	70.9	4,194	2,384.6	71.0
——	——		4,073	2,455.2	
——	——		3,957	2,527.4	
3,863	2,588.7		——	——	
3,757	2,661.7		——	——	
——	——		3,648	2,741.2	

[1] Two bands at 2,604.6 and 2,675.2 are perhaps to be regarded as members of this series but displaced about 10 to the red. They are designated as α'.

We were surprised to find that of eleven bands indicated by them as lying between .4900μ and .6700μ nine might be considered as related to the various series described in the present paper. In the following table the wave-lengths and frequencies of these bands are given together with the frequency of the corresponding member of our series computed on the assumption of its extension towards the red with the constant interval of 71.

Considering that the bands of Jones and Strong are for the simple chloride in solution, it might be held that a comparison with bands of a double chloride in the crystalline form is entirely without significance. It has seemed worth while however to call attention to these approximate coincidences of position.

Table XI. gives the bands thus far located in the absorption spectrum at + 20° C. It will be noted that series γ and δ' disappear after the

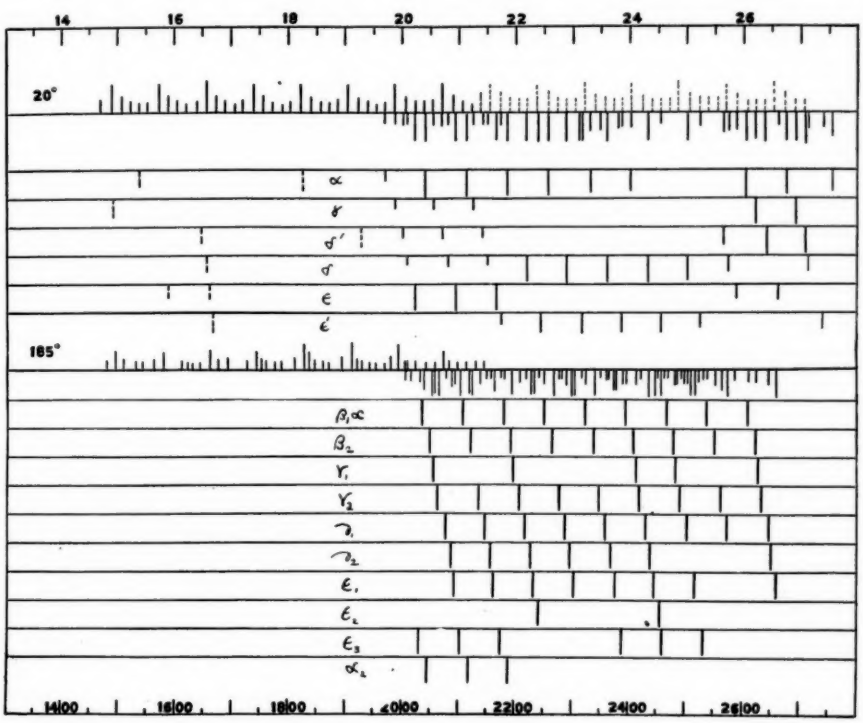


Fig. 7.

third member but reappear in the extreme violet; also that δ, which appears as a doublet with δ' at both ends of the spectrum, continues throughout the wide gap between .47μ and .39μ where γ and δ' are missing.

The absorption spectrum of this salt at $-185°$ undergoes changes strictly analogous to those described in the case of the fluorescence spectrum. There is the usual narrowing of the bands with further resolution. The bands in the absorption spectrum however are still capable of arrangement in series with a nearly constant frequency interval of about 71 and these series in general have their origin in coincidence with a fluorescence series. The apparent exceptions are undoubtedly due to the fact that the bands, both of fluorescence and absorption, are complex and only partially resolved.

The general grouping of the fluorescence and absorption bands at

TABLE XII.

"Fluorescence" Bands of $UO_2Cl_2 \cdot 2NH_4Cl + 2H_2O$ *at* $-185°$ *C. Arranged in Series.*

Series b_1.			Series b_2.		
λ	$1/\lambda \times 10^3$	Average Interval.	λ	$1/\lambda \times 10^3$	Average Interval.
——	——		6,758	1,479.7	
——	——		6,398	1,563.0	
6,110	1,636.7		6,079	1,645.0	
——	——	83.0	5,791	1,726.9	83.2
——	——		5,524	1,810.4	
——	——		5,279	1,894.4	
5,080	1,968.7		5,056	1,977.9	
Series c.			Series d_1.		
6,682	1,496.5		——	——	
6,330	1,579.8		——	——	
6,016	1,662.1		——	——	
5,733	1,744.4	82.6	5,704	1,753.1	83.8
5,471	1,827.7		5,445	1,836.7	
5,234	1,910.6		5,206	1,921.0	
5,018	1,992.7		4,989	2,004.5	
Series d_2.			Series e_1.		
6,628	1,508.9		——	——	
6,283	1,591.5		——	——	
5,968	1,675.6		——	——	
5,677	1,761.4	84.2	——	——	82.4
5,420	1,845.1		5,379	1,859.0	
5,184	1,929.2		5,149	1,941.9	
4,967	2,013.4		4,940	2,024.1	
Series e_2.			Series a.		
6,538	1,529.6		——	——	
6,207	1,611.0		——	——	
5,899	1,695.0	83.3	——	——	83.1
5,624	1,778.1		5,595	1,787.3	
5,370	1,862.0		5,345	1,870.8	
5,141	1,945.0		5,118	1,953.7	

Table XIII.

Absorption Bands of $UO_2Cl_2 \cdot 2NH_4Cl + 2H_2O$ *at* $-185°$ *C. Arranged in Series.*

Series β_{1a}.			Series β_2.		
λ	$1/\lambda \times 10^3$	Average Interval.	λ	$1/\lambda \times 10^3$	Average Interval.
4,906	2,038.5		4,875	2,051.1	
4,742	2,109.0		4,711	2,122.7	
4,587	2,180.2		4,560	2,193.1	
4,443	2,250.9		4,413	2,265.9	
4,305	2,322.8	71.2	4,277	2,338.2	71.5
4,177	2,394.0		4,152	2,408.7	
4,054	2,466.8		4,034	2,479.0	
3,941	2,537.3		3,922	2,550.1	
3,833	2,609.0		3,813	2,622.7	
Series γ_1.			**Series γ_2.**		
4,863	2,056.5		4,843	2,064.7	
——	——		4,680	2,136.5	
4,551	2,197.3		4,530	2,207.3	
——	——		4,389	2,278.3	
——	——	71.5	4,259	2,348.1	71.1
4,146	2,411.9		4,134	2,419.0	
4,028	2,482.5		4,016	2,489.9	
——	——		3,904	2,561.6	
3,808	2,626.3		3,798	2,633.0	
Series δ_1.			**Series δ_2.**		
4,813	2,077.9		4,792	2,086.8	
4,654	2,148.9		4,639	2,155.5	
4,508	2,218.2		4,490	2,227.0	
4,370	2,288.5		4,352	2,298.0	
4,239	2,359.1	71.0	4,222	2,368.3	70.5
4,114	2,430.9		4,102	2,437.9	
3,997	2,502.0		——	——	
3,886	2,573.2		——	——	
3,780	2,645.5		3,774	2,650.0	
Series ϵ_1.			**Series ϵ_2.**		
4,778	2,092.7		——	——	
4,625	2,162.1		——	——	
4,478	2,233.0		4,460	2,242.2	
4,341	2,303.4		——	——	
4,209	2,376.0	70.7	——	——	70.9
4,090	2,445.0		4,073	2,454.9	
3,975	2,515.8		——	——	
——	——		——	——	
3,763	2,657.5		——	——	

TABLE XIII.—*Continued.*

Series ϵ_3.			Series α_2.		
λ	$1/\lambda \times 10^3$	Average Interval.	λ	$1/\lambda \times 10^3$	Average Interval.
4,924	2,031.0		4,889	2,045.5	
4,756	2,102.4		4,724	2,116.9	
4,599	2,174.4		4,571	2,187.7	
——	——		——	——	
——	——	71.4	——	——	71.0
4,188	2,387.5		——	——	
4,066	2,459.7		——	——	
3,951	2,530.7		——	——	
——	——		——	——	

+ 20° and − 185° is shown in Fig. 7 and the bands, arranged by series as determined from the observations at − 185° are given in Tables XII. and XIII. The different series in the absorption spectrum also shown graphically in Fig. 7. The dotted lines in the upper portion of this figure show the positions in which we should expect fluorescence bands to be found if the fluorescence had extended into the violet.

In a recent paper[1] it has been shown that the fluorescence and absorption of these crystals consists throughout of doublets polarized at right angles to each other and unresolved when the spectrum is observed without the aid of a Nicol prism or other analyzer. These polarized spectra and their relation to those described here will be considered in detail in a forthcoming article.

PHYSICAL LABORATORY OF CORNELL UNIVERSITY,
June 2, 1915.

[1] Nichols and Howes, Proceedings of the National Academy of Sciences, Vol. 1, p. 444.

THE VARIATION OF THE SPECIFIC HEAT OF SOLIDS WITH TEMPERATURE.

BY ARTHUR H. COMPTON.

THE very considerable success of the quantum hypothesis in explaining the variations of the specific heat of solids with temperature has been taken as a strong confirmation of that hypothesis. Before this evidence can be considered as conclusive, however, it is necessary to see if there may not be some other satisfactory solution of the problem of specific heat, which does not involve the conception of quanta. It has been pointed out by several writers[1] that the sharp decrease of the specific heat of solids at low temperatures can be qualitatively explained if it is assumed that at these temperatures the atoms become so intimately associated that degrees of freedom are lost. In fact Benedicks[1] has been able to obtain an empirical expression on this assumption which, with properly chosen constants, fits the experimental data acceptably. In the present paper an assumption is introduced which leads directly to an expression for the variation of the specific heat with temperature which will be shown to agree at least as well with experiment as the expressions derived from the quantum hypothesis.

The assumption on which the following work is based is:

If the relative energy between two neighboring atoms in a solid falls below a certain critical value, the two atoms become agglomerated[2] so that the degree of freedom between them vanishes; but as soon as the energy increases again above the critical value, the degree of freedom reappears.

The defence of this assumption from various lines of evidence will form the subject of a later paper.

DERIVATION OF A FORMULA FOR THE SPECIFIC HEAT.

The energy content of the unagglomerated degrees of freedom may be written, according to equipartition,

$$U_u = nRT,$$

[1] F. Richarz, Zeitschr. f. anorg. Chem., 58, 356; 59, 146. J. Duclaux, Compt. Rend., 155, 1015. C. Benedicks, Ann. d. Phys., 42, 133.

[2] The term "agglomeration," suggested by Benedicks, is used to indicate any state of association of the atoms on account of which degrees of freedom for thermal motion disappear.

where n is the number of unagglomerated degrees of freedom, R the gas constant for a single molecule, and T the absolute temperature. In the case of the chemical combination of two atoms, when a degree of freedom vanishes its energy is usually transmitted to the other degrees of freedom in the form of heat of formation. In the case of endothermic substances, however, the vanishing degree of freedom absorbs a certain amount of energy. We may assume provisionally, therefore, that when two atoms in a solid agglomerate they retain a certain amount of potential energy. The amount of this energy will be,

$$U_a = \gamma(3N - n),$$

where γ is the potential energy of each agglomerated degree of freedom, and $3N$ is the greatest possible number of degrees of freedom. The total energy content of the solid is therefore,

$$U = U_u + U_a = nRT + \gamma(3N - n).$$

If we call P the probability that a certain possible degree of freedom shall actually exist, $P = n/3N$, and

$$U = 3NRTP + 3N\gamma(1 - P). \tag{1}$$

In the case of a solid the kinetic energy of a degree of freedom is on the average equal to its potential energy. We may assume, therefore, that the probability for a certain value of the potential energy is equal to the probability for the same value of the kinetic energy. By Maxwell's distribution law, the probability that the relative velocity of two atoms along the line of their centers shall lie between $| u |$ and $| u + du |$ is

$$\frac{2}{\alpha\sqrt{\pi}} e^{-\frac{u^2}{\alpha^2}} du,$$

where

$$\alpha = 2\sqrt{\frac{RT}{m}}.$$

This is therefore also the probability that the relative kinetic energy shall lie between $\frac{1}{2}mu^2$ and $\frac{1}{2}m(u + du)^2$. Since the probability for the potential energy is equal to that for the kinetic energy, the probability that the relative potential energy shall lie between $\frac{1}{2}mv^2$ and $\frac{1}{2}m(v + dv)^2$ is similarly,

$$\frac{2}{\alpha\sqrt{\pi}} e^{-\frac{v^2}{\alpha^2}} dv.$$

Thus the probability that the total energy shall lie between $\frac{1}{2}m(u^2 + v^2)$ and $\frac{1}{2}m\{u^2 + v^2 + d(u^2 + v^2)\}$ is the product of these two expressions, or

$$\frac{4}{\alpha^2\pi} e^{-\frac{u^2}{\alpha^2}} e^{-\frac{v^2}{\alpha^2}} du dv.$$

If we let ϵ be the critical value of the energy below which a degree of freedom remains agglomerated, the probability that the degree of freedom shall be agglomerated is:

$$P' = \int_0^{\frac{1}{2}m(u^2+v^2)=\epsilon} \frac{4}{\alpha^2\pi} e^{-\frac{u^2}{\alpha^2}} e^{-\frac{v^2}{\alpha^2}} du dv,$$

$$= \frac{4}{\alpha^2\pi} \int_0^{u^2=\frac{2\epsilon}{m}} e^{-\frac{u^2}{\alpha^2}} du \int_0^{v^2=\frac{2\epsilon}{m}-u^2} e^{-\frac{v^2}{\alpha^2}} dv,$$

or

$$= \frac{4}{\alpha^2\pi} \int_0^{\beta} e^{-\frac{u^2}{\alpha^2}} du \int_0^{\sqrt{\beta^2-u^2}} e^{-\frac{v^2}{\alpha^2}} dv;$$

where

$$\beta^2 = \frac{2\epsilon}{m}.$$

This integral may be determined by a series method, the solution being,

$$P' = \frac{\beta^2}{\alpha^2} - \frac{1}{2!}\frac{\beta^4}{\alpha^4} + \frac{1}{3!}\frac{\beta^6}{\alpha^6} - \cdots.$$

This is the probability that a possible degree of freedom shall be agglomerated. The probability that it shall actually exist is therefore:

$$P = 1 - P'$$

$$= 1 - \frac{\beta^2}{\alpha^2} + \frac{1}{2!}\frac{\beta^4}{\alpha^4} - \frac{1}{3!}\frac{\beta^6}{\alpha^6} + \cdots.$$

But

$$e^{-\frac{\beta^2}{\alpha^2}} = 1 - \frac{\beta^2}{\alpha^2} + \frac{1}{2!}\frac{\beta^4}{\alpha^4} - \frac{1}{3!}\frac{\beta^6}{\alpha^6} + \cdots,$$

and by comparison of series,

$$P = e^{-\frac{\beta^2}{\alpha^2}}.$$

We may substitute for β^2/α^2 its equivalent,

$$\frac{\beta^2}{\alpha^2} = \frac{\frac{2\epsilon}{m}}{\frac{4RT}{m}} = \frac{\epsilon}{2RT} = \frac{\tau}{T}, \quad \text{where} \quad \tau = \frac{\epsilon}{2R},$$

then

$$P = e^{-\frac{\tau}{T}}. \tag{2}$$

Substituting this value of P in equation (1) we have:

$$U = 3NRTe^{-\frac{\tau}{T}} + 3N\gamma(1 - e^{-\frac{\tau}{T}}), \tag{3}$$

and the specific heat is:

$$C_v = \frac{dU}{dT} = 3NRe^{-\frac{\tau}{T}} + \frac{3NR\tau}{T}e^{-\frac{\tau}{T}} - 3N\gamma\frac{\tau}{T^2}e^{-\frac{\tau}{T}}. \tag{4}$$

Since there is a T^2 in the denominator of the last term, it is evident that as long as γ has a finite value, T can be made so small that C_v will become negative. This is impossible, as it implies a condition of instability, so we must place $\gamma = 0$, and

$$C_v = 3NRe^{-\frac{\tau}{T}}\left(\frac{\tau}{T} + 1\right). \tag{5}$$

If $T = \infty$, $C_v = 3NR = C_\infty$,

$$\therefore \frac{C_v}{C_\infty} = e^{-\frac{\tau}{T}}\left(\frac{\tau}{T} + 1\right). \tag{6}$$

This is the expression for the variation of the specific heat with temperature to which our assumption leads.

TESTING THIS EQUATION.

The curves of Fig. 1 show how this formula compares with that of Debye for the specific heat.[1] The solid line is plotted from equation (6)

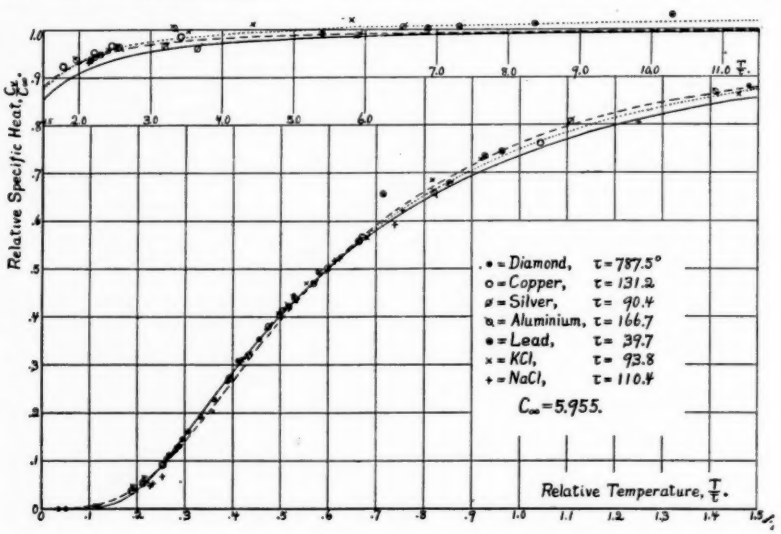


Fig. 1.

and the broken one from Debye's equation,

$$\frac{C_v}{C_\infty} = \frac{12}{x^3}\int_0^x \frac{\xi^3 d\xi}{e^\xi - 1} - \frac{3x}{e^x - 1},$$

where $x = \Theta/T$. The two curves have been made to coincide at $C_v/C_\infty = 0.5$. That they are in general good agreement is evident at a glance.

[1] Debye, Ann. d. Phys., 39, 789. Debye's formula is used because his has been shown to be the most accurate of any of the existing expressions (cf. E. H. Griffiths and E. Griffiths, Proc. Roy. Soc., A, 90, 558).

Their comparative accuracy has been tested with the data used by Debye and by Nernst and Lindemann[1] in testing their own formulæ. I have taken their calculations of C_v from the observed value of C_p. The value of γ for each of the substances is chosen so as to bring the experimental values as near as possible to the two curves where they cross.[2]

At lower temperatures, though the curves are not far apart, there is an evident preponderance of experimental evidence in favor of the solid curve. Above $T/\tau = 0.6$, however, the experimental values gradually rise from the solid curve, cross the broken one at about 2.25, and continue approximately parallel to the solid curve but at a higher level. The dotted curve is drawn as an approximate experimental mean. It is evident that the data fit neither formula accurately for these temperatures, but that the values of C_v/C_∞ approach a limit some two per cent. higher than unity. That these high values of C_v are not due to proximity to the melting point is evident when one notices that none of the experiments are made at a temperature closer than 191° to the melting point, while in the case of KCl the value of C_v/C_∞ rises above unity when the temperature is only .40 as high as the melting point. A possible explanation of the high values of the specific heat at these temperatures is that there may be more degrees of freedom in a solid than indicated by Rayleigh's formula, $C_\infty = 3R$. Whatever the cause of this discrepancy, however, it is necessary on any theory that C_v shall never become greater than C_∞, so we must assume a value of C_∞ greater than $3R = 5.955$, which is the value used in calculating the values of C_v/C_∞ in Fig. 1. The value 6.081 has therefore been chosen as an experimental limit which C_v seems to approach.

Fig. 2 shows the same theoretical curves and the experimental data plotted with this new value of C_∞. The curves have here been made to coincide at $C_v/C_\infty = 0.65$, in order to show more clearly the differences between the two formulæ. It will be seen that this correction makes the observed specific heats conform very well with the curve plotted according to my expression, while they vary consistently from that of Debye. Thus while the data can in no way be made to conform at all temperatures with Debye's formula, by making a correction which would seem necessary in any case, the data may be made to fit well the equation

[1] Zeitschr. für Electrochemie, 17, p. 817.

[2] In the following tables the values of C_v for Al, Pb, KCl and NaCl are taken from Nernst and Lindemann's paper (*loc. cit.*), those for Cu, Ag and diamond from that of Debye (*loc. cit.*). C_v is calculated from the observed values of C_p according to the formula, due to Nernst and Lindemann, $C_v = C_p - 0.0214 C_p^2 T/T_s$, where T_s is the melting point of the substance. C_∞ is taken to be 6.081 as explained in the text.

T	C_v Obs.	C_v Calc.
Diamond, $\tau = 794.0°$		
30°	0.00	0.00
42	0.00	0.00
88	0.03	0.01
92	0.03	0.015
205	0.62	0.63
209	0.66	0.67
220	0.72	0.75
222	0.76	0.80
232	0.86	0.87
243	0.95	0.98
262	1.14	1.18
284	1.35	1.41
306	1.58	1.60
331	1.83	1.87
358	2.11	2.13
413	2.64	2.62
1169	5.24	5.18
Copper, $\tau = 133.5°$		
23.5°	0.22	0.14
27.7	0.32	0.26
33.4	0.54	0.56
87	3.32	3.32
88	3.37	3.36
137	4.53	4.54
234	5.50	5.40
290	5.66	5.60
323	5.75	5.69
450	5.87	5.86
Lead, $\tau = 38.4°$		
23.0°	2.95	3.04
28.3	3.91	3.69
36.8	4.38	4.38
38.1	4.43	4.45
85.5	5.57	5.60
90.2	5.63	5.67
200	5.91	5.98
273	5.99	6.02
290	5.99	6.02
332	6.03	6.03
409	6.15	6.05
Silver, $\tau = 92.0°$		
35.0°	1.58	1.58
39.1	1.90	1.93
42.9	2.26	2.25

T	C_v Obs.	C_v Calc.
Silver (continued)		
45.5°	2.46	2.44
51.4	2.80	2.83
53.8	2.89	2.98
77.0	4.04	4.04
100	4.80	4.65
200	5.61	5.61
273	5.75	5.79
331	5.71	5.87
535	5.90	5.93
589	5.99	5.99
Aluminum, $\tau = 169.6°$		
32.4°	0.25	0.19
35.1	0.33	0.28
83.0	2.40	2.40
86.0	2.51	2.51
88.3	2.61	2.60
137	3.91	3.94
235	5.17	5.09
331	5.58	5.55
433	5.74	5.72
555	5.98	5.85
NaCl, $\tau = 113.5°$		
25.0°	0.29	0.36
25.5	0.31	0.38
28.0	0.40	0.52
67.5	3.05	3.04
69.0	3.12	3.10
81.4	3.52	3.60
83.4	3.72	3.71
138	4.79	4.87
235	5.55	5.57
KCl, $\tau = 96.1°$		
26.9°	0.76	0.78
33.7	1.25	1.35
39.0	1.83	1.80
52.8	2.79	2.78
63.2	3.34	3.34
76.6	4.08	3.91
86.0	4.33	4.22
137	5.18	5.15
235	5.73	5.69
331	5.93	5.87
416	6.02	5.95
550	6.09	5.99

just derived. In fact, all variations from the theoretical values seem to lie within the limits of experimental error.

DISCUSSION OF THE FORMULA.

Some interesting aspects of formula (6) appear if the exponent of e is written in a different form. τ is defined as $\epsilon/2R$, where ϵ is the energy required to liberate an agglomerated degree of freedom. This quantity has the same dimensions as Planck's energy quantum $h\nu$, both being elementary units of energy. In fact Benedicks has shown,[1] from a consideration of the relation of hardness to the frequency of vibration of an atom, that ϵ is probably proportional to ν. If we call the factor of proportionality b, the probability becomes

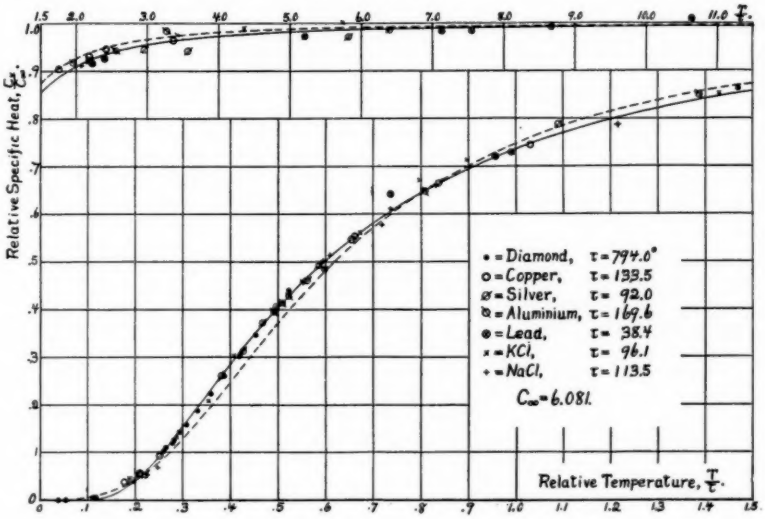


Fig. 2.

(7) $$P = e^{-\frac{\tau}{T}} = e^{-\frac{\epsilon}{2RT}} = e^{-\frac{b\nu}{2RT}} = e^{-\frac{\beta\nu}{T}},$$

where

$$\beta = \frac{b}{2R}.$$

The value of β can easily be determined from the expression $\beta = \tau/\nu$, which follows from equation (7). The values of τ for the different substances considered are determined by their specific heats as shown in Fig. 2. The values of ν may be taken as those assigned by Nernst and Lindemann's formula for the specific heat, since their values of ν have been shown to be in very accurate agreement with the characteristic

[1] *Loc. cit.*

frequencies of those substances whose reststrahlen can be obtained. The different values of β as thus determined are given in the following table.

Substance.	τ	$\nu \times 10^{-12}$	$\beta \times 10^{11}$	Difference from Mean.
Lead	38.4	1.9	2.02	+0.3%
Silver	92.0	4.5	2.04	+1.4
KCl	96.1	4.73	2.03	+0.6
NaCl	113.1	5.8	1.96	−2.9
Copper	133.5	6.6	2.02	+0.3
Aluminium	169.6	8.3	2.04	+1.4
Diamond	794.0	40.0	1.98	−1.4

β is thus determined just as accurately as ν is known, and since it remains constant over so great a range of frequencies, equation (7) may be considered valid, even though its derivation is not rigid.

It is interesting to see how the quantity b in this equation compares with the similar quantity h of Planck's expression. b is determined by the equation $b = 2R\beta$, in which the accepted value of R is about 1.35×10^{-16} erg deg.$^{-1}$, and $\beta = 2.01 \times 10^{-11}$ deg. sec. Thus

$$b = 5.44 \times 10^{-27} \text{ erg sec.},$$

while Planck's constant h has the value

$$h = 6.55 \times 10^{-27} \text{ erg sec.}$$

The value for b found here is in excellent agreement with certain values of h as determined by photoelectric methods: Richardson and Compton[1] 5.4×10^{-27}; Hughes[2] 5.6×10^{-27}; Cornelius[3] 5.7×10^{-27}; though Kadesch[4] and Millikan[5] very recently have obtained photoelectric values of h more nearly 6.55×10^{-27}.

Now that equation (7) has been established we are in a position to make a new application of Debye's theory which interprets the heat energy of solids in terms of their elastic vibrations. He considers a whole spectrum of frequencies, the number of vibrations between the frequencies ν and $\nu + d\nu$ being

$$dn = \frac{9N}{\nu_m^3} \nu^2 d\nu, \tag{8}$$

[1] Phil. Mag., 24, 574.
[2] Phil. Trans. Roy. Soc., 212, 205.
[3] K. T. Compton, PHYS. REV., 1, 382.
[4] PHYS. REV., 3, 367.
[5] PHYS. REV., 4, 73.

where $3N$ is the total number of degrees of freedom in the solid, and ν_m is the maximum possible frequency, determined by the equation:

$$(9) \qquad \frac{1}{\nu_m^3} = \frac{4\pi V}{9N}\left\{ 2\left(\frac{2\rho(1+\sigma)\chi}{3(1-2\sigma)}\right)^{\frac{3}{2}} + \left(\frac{2\rho(1+\sigma)\chi}{3(1-\sigma)}\right)^{\frac{3}{2}} \right\},$$

where V is the volume, ρ the density, χ the compressibility, and σ Poisson's ratio, for the substance considered. The average energy of a degree of freedom of frequency ν is, by equations (3) and (7),

$$(10) \qquad \frac{3NRTe^{-\frac{\beta\nu}{T}}}{3N} = RTe^{-\frac{\beta\nu}{T}};$$

so the total energy in the solid is

$$U = \int_0^{\nu_m} \frac{9N}{\nu_m^3}\nu^2 \cdot RTe^{-\frac{\beta\nu}{T}},$$

$$= \frac{9NRT}{\nu_m^3}\left\{ \frac{2T^3}{\beta^3} - e^{-\frac{\beta\nu_m}{T}}\left(\frac{T}{\beta}\nu_m^2 + \frac{2T^2}{\beta^2}\nu_m + \frac{2T^3}{\beta^3}\right)\right\}.$$

Substituting $\tau = \beta\nu_m$,

$$U = 9NRT\left\{ \frac{2T^3}{\tau^3} - e^{-\frac{\tau}{T}}\left(\frac{T}{\tau} + \frac{2T^2}{\tau^2} + \frac{2T^3}{\tau^3}\right)\right\}.$$

According to Debye's assumptions ν_m, and hence also τ, are not functions of T, so the specific heat is:

$$C_v = \frac{dU}{dT} = 9RN\left\{ 8\frac{T^3}{\tau^3} - e^{-\frac{\tau}{T}}\left(8\frac{T^3}{\tau^3} + 8\frac{T^2}{\tau^2} + 4\frac{T}{\tau} + 1\right)\right\},$$

and

$$(11) \qquad \frac{C_v}{C_\infty} = 3\left\{ 8\frac{T^3}{\tau^3} - e^{-\frac{\tau}{T}}\left(8\frac{T^3}{\tau^3} + 8\frac{T^2}{\tau^2} + 4\frac{T}{\tau} + 1\right)\right\}.$$

Fig. 3 shows how this expression compares with equation (6). The solid line as before represents the first equation derived, while the broken one represents equation (11). Although the difference between these two curves is not large, it is evident, particularly at low temperatures, that this new formula does not represent the facts accurately. It is necessary to conclude, therefore, either that the energy of each degree of freedom is not accurately expressed by equation (10) or that some of the assumptions on which Debye's theory is based are not valid.

It is evident that if equation (11) is to be valid, ν_m must not vary with the temperature. That is, by equation (9), the quantities σ and χ must be independent of the temperature. While there is no evidence of any considerable variation in the value of σ, Grüneisen has shown[1]

[1] Ann. d. Phys., 33, 1239. Some of Grüneisen's results indicating such a variation of the compressibility with the temperature may be given:

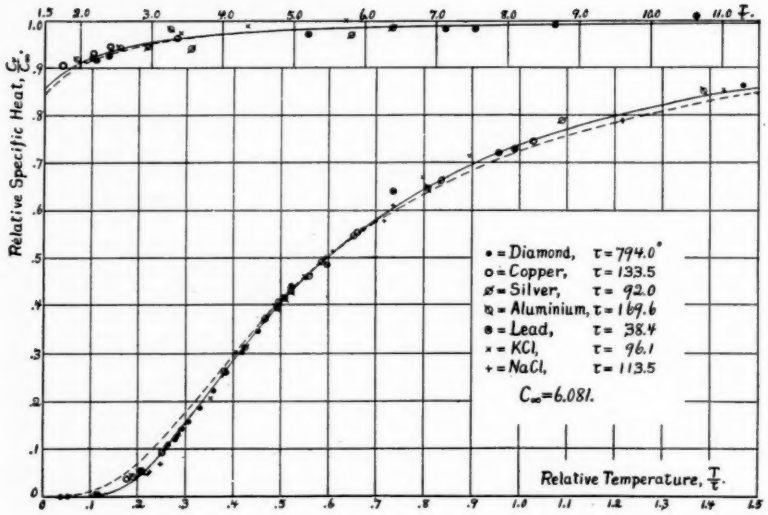

Relative Specific Heat, $\frac{C_v}{C_\infty}$
Relative Temperature, $\frac{T}{\tau}$
• = Diamond, τ = 794.0°
o = Copper, τ = 133.5
ø = Silver, τ = 92.0
a = Aluminium, τ = 169.6
• = Lead, τ = 38.4
× = KCl, τ = 96.1
+ = NaCl, τ = 113.5
C_∞ = 6.081.

Fig. 3.

Compressibility × 10_6.

T	Al	Fe	Cu	Ag	Pt	Sn	Pb
83°	1.32	0.606	0.718	0.709	0.374	2.1	2.5
290	1.46	0.633	0.773	0.763	0.392	3.1	3.2
373	1.70	0.652	0.801	0.820	0.398	—	—

that there is a general and decided increase in the compressibility χ with the temperature. It is evident, therefore, that account must be taken of the variation of ν_m with the temperature. If this is done, equation (11) becomes:

$$\frac{C_v}{C^\infty} = 3\left\{8\frac{T^3}{\tau^3} - e^{-\frac{\tau}{T}}\left(8\frac{T^3}{\tau^3} + 8\frac{T^2}{\tau^2} + 4\frac{T}{\tau} + 1\right)\right.$$
$$\left. - \left[6\frac{T^4}{\tau^4} - e^{-\frac{\tau}{T}}\left(6\frac{T^4}{\tau^4} + 6\frac{T^3}{\tau^3} + 3\frac{T^2}{\tau^2} + \frac{T}{\tau}\right)\right]\frac{d\tau}{dT}\right\}.$$

The order of magnitude of $d\tau/dT$ is 5×10^{-4}, so the last term is negligible except at high temperatures; but instead of considering τ to be constant, its particular value which corresponds to the temperature for which C_v/C_∞ is evaluated must be employed in order to make equation (11) valid. In the case of aluminum, for example, the compressibility at 373° is 29 per cent. greater than at 83°. This corresponds to a difference in ν_m, and hence also in τ of 13.5 per cent., and in the specific heat at the lower temperature of about 45 per cent. Thus if the specific heat of aluminum at 83° is calculated from its elastic constants at 373°

the resulting value is some 45 per cent. greater than if calculated from its constants at the lower temperature. This shows conclusively that equation (11) is not valid if τ is considered independent of the temperature.

That the same argument applies to Debye's formula for the specific heat is shown by the form of his equation at low temperatures,

$$\frac{C_v}{C_\infty} = 77{\cdot}93\frac{R^3T^3}{h^3\nu_m^3}.$$

In this equation the value of the ratio C_v/C_∞ for aluminum varies 46 per cent. according as the value of ν_m is calculated from the elastic constants at 373° or at 83°. It is thus evident that the error introduced by Debye's assumption that ν_m is independent of the temperature is much too large to be neglected.

It can be shown, moreover, that the fundamental assumption on which Debye's theory is based, that the heat energy of a solid lies in the elastic vibrations of the body as a whole, does not represent the truth. It may be shown that the velocity of propagation of a thermal disturbance in a solid is directly proportional to the diameter of the elementary vibrator. If, as Debye assumes, the whole substance is capable of vibrating as a unit in its heat motion, the thermal conductivity should therefore be very great. This may be shown more clearly in the following manner. Consider two infinite parallel planes in an elastic medium, at one of which the medium is maintained with vibrational energy greater than at the other corresponding to a difference in temperature of one degree. The thermal conductivity, or rate at which energy is transmitted from the hotter to the colder plane per unit area will then be equal to the product of the difference in the energy content of the medium at the two planes by the velocity of transmission of the vibrational disturbance; *i. e.*:

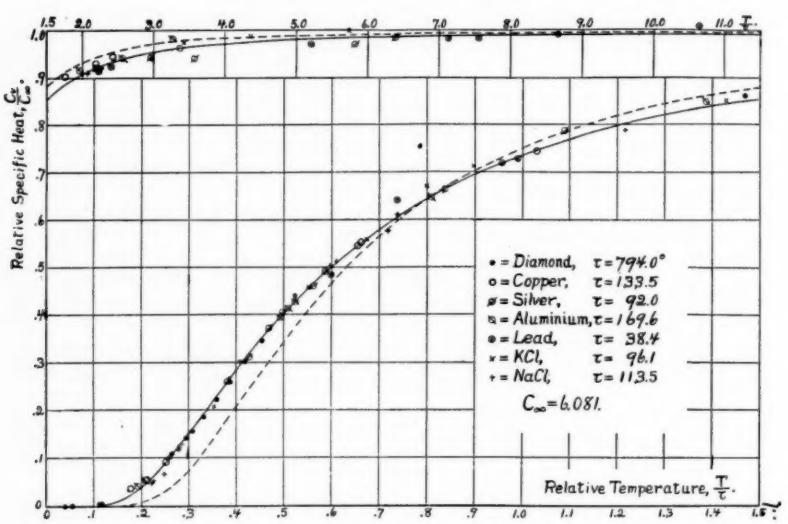
$$\text{thermal conductivity} = V \cdot C(t_1 - t_2) = V \cdot C,$$

where C is the heat capacity per unit volume of the medium, and V is the mean velocity of propagation of a vibrational disturbance. For aluminum C is about 0.5 calories cm.$^{-3}$ deg.$^{-1}$, and V may be taken as about 5×10^6 cm. sec.$^{-1}$, so the thermal conductivity should be of the order of magnitude of 2.5×10^5 calories cm.$^{-2}$ sec.$^{-1}$ deg.$^{-1}$. This is wholly out of accord with the experimental value, which is 0.5 calories cm.$^{-1}$ sec.$^{-1}$ deg.$^{-1}$. In fact the dimensions themselves are different, the rate of heat transmission according to this assumption being independent of the distance apart of the two parallel planes. It is evident,

therefore, that the heat energy of solids is not contained in the elastic vibrations of the body as a whole, but is contained in the motion of very much smaller elements. Since the lower limit of the frequencies which enter into Debye's theory is determined by the dimensions of the vibrator, the range of frequencies in which thermal motion occurs is thus limited. If the elementary vibrator is of atomic dimensions, the only frequencies to be considered are the natural frequencies of the atoms themselves.[1] Thus the assumption that thermal motion occurs in all the possible frequencies from o to ν_m cannot be accepted.

Debye's formula for the specific heat must therefore be considered to be largely empirical. In order to compare the results of this agglomeration hypothesis with those of the quantum hypothesis, equation (6) should be compared rather with Einstein's formula,[2]

$$\frac{C_v}{C_\infty} = \frac{h^2\nu^2}{R^2T^2}\,\frac{e^{h\nu/RT}}{(e^{h\nu/RT}-1)^2},$$


Relative Specific Heat, $\frac{C_v}{C_\infty}$.
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a = Aluminium, τ = 169.6
• = Lead, τ = 38.4
× = KCl, τ = 96.1
+ = NaCl, τ = 113.5
C_∞ = 6.081.

Fig. 4.

which is a valid deduction from the quantum hypothesis. Fig. 4 shows how these two expressions compare. The solid line represents my

[1] The great increase in thermal conductivity at low temperatures may be shown to indicate that the diameter of the elementary vibrator becomes comparatively large at low temperatures. Under these circumstances Debye's assumption of a whole spectrum of frequencies may be valid. This may account for the fact that at extremely low temperatures, $T/\tau = o$ to 0.22, the observed specific heats are slightly larger than indicated by equation (6). If this be true, equation (11) should hold at these temperatures, and Debye's "third power law" would still be true.

[2] Einstein, Ann. d. Phys., *22*, 180.

formula and the broken one that of Einstein. The experimental values are the same as in Fig. 2. It is evident that Einstein's expression is much the less accurate of the two. Thus from the standpoint of the variation of specific heat with temperature the assumption is strongly supported that at sufficiently low temperatures many of the atoms of a solid become so intimately associated that they lose degrees of freedom.

SUMMARY.

The assumption has been made that a possible degree of freedom between two atoms in a solid actually exists only as long as the relative energy between the two atoms is greater than a certain critical value.

An expression for the variation of the specific heat of solids with temperature has been derived from this assumption, which seems to agree more satisfactorily with experiment than any of the existing formulæ.

Debye's expression for the variation of the specific heat with temperature has been found to be largely empirical; so to compare this agglomeration hypothesis with the quantum hypothesis my formula is rather to be compared with that of Einstein.

The strong support of experimental evidence in this case seems to indicate that this agglomeration hypothesis represents more accurately the condition of the atoms in a solid than does the quantum hypothesis.

I wish to express my thanks to Professor Adams and Professor Magie for their continued interest in this study.

PALMER PHYSICAL LABORATORY,
PRINCETON, N. J.,
May 5, 1915.

A HIGHLY SENSITIVE ELECTROMETER.

BY A. L. PARSON.

FOR the measurement, and more particularly the detection, of very small potential differences on open circuit a very highly sensitive electrometer was required. The most sensitive hitherto described is the "duant" electrometer of Hofmann[1] which has a capacity of only 5 cm. and may be adjusted to work in a condition approaching instability. It can then give deflections at the rate of 10 mm. per millivolt (scale distance 1.5 meters), but he does not state whether it is steady enough in its action to detect a single 10^{-4} volt unit by a 1 mm. deflection, the only results given from which the steadiness can be judged being for the lower sensitivity of 1 *mm/mv*. This instrument suffers from the disadvantage of requiring a needle of extremely delicate and exact construction, but a more troublesome feature is the complexity of the electrical system used in its operation. The suspension is made conducting and the potential to be measured is communicated to the needle, while the two conductors which take the place of quadrants must be kept at a high potential difference by a constant battery: it is by a careful adjustment of this potential difference that the maximum sensitivity is obtained.

The principle of working with a condition approaching instability has also been used greatly to increase the sensitivity of the gold-leaf electroscope by C. T. R. Wilson, and of the string electrometer by Wulf, but neither of these has the inherent sensitivity of the suspended needle electrometer, of which the most familiar form is of course that of Dolezalek. This instrument, in its ordinary form, can give, with very fine quartz fibers, deflections at the rate of 10 mm. per millivolt, but is then somewhat uncertain and slow in its action. Its capacity is about 50 cm. and probably could not be made less without diminishing its sensitivity to potential differences. The necessity of securing a uniform inducting surface inside the quadrants also makes against a small capacity, for the gaps must be small and the quadrant edges thick.

[1] Ann. d. Phys. [4], 42, pp. 1196–1220, 1913.

The Principle of the Instrument.

The instrument about to be described is a modification of the quadrant electrometer, which does not suffer from these disadvantages, and which by an ability to work in a condition approaching instability can be made very much more sensitive. To a certain extent, however, it loses the good feature of giving a deflection proportional to the potential difference.

The four quadrants are replaced by four sectors arranged in pairs AB, $A'B'$, as in Fig. 1, and the box form of the quadrants is abandoned, the sectors being cut from a single disc of metal .5 mm. thick. In the quadrant electrometer the torsion of the quartz fiber is used as a measure of the force on the needle, and is the only source of its stability: in the present case, however, the stability of the needle is procured by an automatic disposition of electric forces; and the torsion of the fiber is useful only for balancing any disymmetry in the electric forces such as may arise from a slightly uneven mounting of the sectors. In the more sensitive adjustments of the instrument, however, this control by the torsion head is very valuable.

Fig. 1.

As regards the electrical connections, the instrument can be used in exactly the same way as the quadrant electrometer, and the needle can be charged either by a constant battery through a conducting suspension, or by the simpler method of a charging switch.

The chief innovation is that the sectors are mounted on a pair of arms pivoted scissors-like at the center, and that the small gaps between A and B, A' and B' can be varied in width from something very small to about 2 mm. by the action of a micrometer screw. When the gap is small and the sectors are at equal potentials, A and B form a virtually continuous inducing surface opposite the charged needle and the capacity of the system is highest when the needle hangs symmetrically over them: this therefore is its stable position. If a difference of potential is set up between AA' and BB', the needle is deflected, at first nearly proportionally to the potential difference, and then less and less as it approaches the large gaps at the sides. This is the least sensitive way of using the instrument, and gives deflections at the rate of about 3 mm. per millivolt (the scale being 5 meters distant[1]). As the gap between A and B is

[1] It was found possible to use this great scale distance profitably by placing the telescope near the instrument and at an angle. If the plane of incidence of the light on the mirror is horizontal, the scale divisions are blurred owing to reflection at both the surfaces of the mirror glass; but if the plane is vertical, as when the scale is placed high up and the telescope is inclined upwards towards the mirror, this does not occur. The increased sensitivity due to the use of this greater scale distance is valuable in itself, but is not of course a property of

widened, the needle becomes less and less stable in its central position and the sensitivity greater and greater. Just before instability is reached a stable deflection at the rate of as much as 150 mm. per millivolt can be obtained, but it is probably not worth while working with deflections greater than about 40 mm. per millivolt, as will appear later.

It is of interest to notice that when the sectors are very close, and the instrument least sensitive, the sensitivity increases as the potential to which the needle is charged diminishes. This might have been predicted, for, while the deflecting force is proportional to the first power of the charge on the needle, the electrical force giving it stability is more nearly proportional to the square of it. Some values got with an older model, in which the needle was 3 cm. long and the quartz fiber thin enough for its torsion to be almost negligible, are as follows:

Potential of needle in volts	80	40	20	10
Deflection in mm. per millivolt	2.1	3.8	5.3	9

But there is no advantage in using the lower potentials, for the maximum sensitivity attainable is not at all increased, while the period of deflection is greatly lengthened. All the results given in this paper were got with a needle potential of + 80 volts. (The fact that a positive charge is lost to the air less rapidly than a negative one was pointed out in connection with electrometers by Lord Kelvin: the difference cannot be great at 80 volts, however.)

One of the chief advantages of this instrument is that its sensitivity to potential differences is quite independent of the scale on which it is built, for the torsion of the suspension is not a determining factor unless it is altogether too thick. As it is easy to get a quartz fiber .002 mm. thick, which would suit a needle .5 cm. long, it is evident that the capacity can be made very small. Actually, the limiting factor is the smallest mirror with which a scale can be read at a distance of say 1 meter. This is about 2 mm. square and would have too great a moment of inertia for a needle less than about .7 cm. long. In a trial instrument the needle was 3 cm. long, but in the one now to be described it is 1.8 cm., and the disc from which the sectors were cut was 2.1 cm. in diameter, with a .75 cm. hole in its center. The capacity was found to be 9 cm. by a method of induction through a condenser of known and variable capacity.

CONSTRUCTIONAL DETAILS (FIG. 2).

The most convenient arrangement of parts was found to be given by making a base *A* (carrying the sectors and provided with suitable widely-

the electrometer. To compare with Hofmann's result of 10 mm. per millivolt, for example, which was got at a scale distance of 1.5 meters, the sensitivity values here given should be divided by 3.3. Hofmann used a spot of light instead of a reading telescope and read the scale to .5 mm. only.

spread feet) to which the rest of the instrument (all in one piece) was attached by a spring fit of its cylindrical case *B* around a flange at *C*. The case, which is only 5 cm. in diameter and 4.5 cm. high, is made small in order to diminish the effect of air currents within it, even though the electrical capacity may thus be raised by a unit or so.

The micrometer screw and terminal could be made to come up from below; but this would be inconvenient on so small a scale, and hence they are fixed in curved pads *D* (of brass and vulcanite respectively) which are attached to the base and rest tightly over slots *E* in the cylindrical case when this is pressed down into position. A good fit here is essential in order to avoid disturbance from air-currents.

For the window, which is 1.5 cm. square, a microscope cover slip was found to be optically satisfactory, although a piece of a slide was not. As the window opening is a possible source of electrical disturbance, it is provided with a divergent metal shade *S* projecting 2 cm. This has the further advantage of partly protecting the interior from light: it was noticed that the light (or heat) from a 40-watt lamp at a meter's distance, suddenly falling on the interior, gave rise to a very marked disturbance.

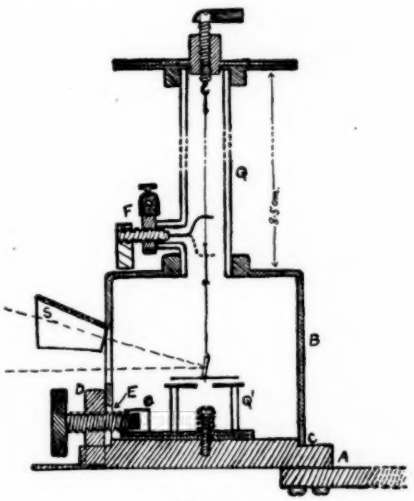

Fig. 2.

The torsion head, which is of any suitable construction, is supported on a quartz tube *Q* fixed to the top of the case. The use of quartz here serves the double purpose of insulating the torsion head (if this should ever be required) and of reducing to a minimum the effect of temperature changes on the distance between the needle and the sectors. This effect would be expected to give more trouble in the present instrument than in one where the needle hung midway between the upper and lower surfaces of quadrants, but it is not yet certain that the precaution is necessary in practice. Since in the ordinary use of the instrument, the exact potential of the needle is not important, provided it remains constant, the needle is charged by means of a switch *F*, which comes through a side tube on the quartz column, and by a rotary motion brings a platinum wire into contact with the lower hook (also of platinum) of the suspension. A light metal shield slipped over the lower part of the quartz tube gives electrical protection at this point.

As regards the insulation, the use of sulphur is difficult on so small a scale, but if the interior is kept dry, clean quartz serves the purpose very well (with phosphorus pentoxide in the case, which it should be said was shown in this way to be by no means impervious to moist air, charge was lost at the rate of about 1 per cent. per minute).[1] Two of the sectors are therefore mounted by means of sealing wax on small quartz rods Q' set on one of the scissors arms, and are connected to the terminal by a fine wire which is previously soldered to them and enters the case through a narrow quartz tube. The other two are soldered to short lengths of wire, and not insulated. Quite the most troublesome part of the whole construction was the setting of the four sectors accurately in one plane parallel to the base, and at the right distances apart.

The micrometer screw may operate by a cone and jaws arrangement but in the present case the end of the screw is squared off and works between glass plates G set at an angle on the arms carrying the sectors.

The needle can be made from a single thickness of thin paper rubbed with graphite on both sides, but the use of the drying agent is then liable to alter its shape; so recourse is had to aluminium. It is made very light by using very thin foil and then by thinning the two ends by dipping in hydrochloric acid until they begin to show signs of disintegration. In this way the weight has been reduced to 3 mgm. The weight of the mirror (10 mgm.) is less important on account of its smaller moment of inertia, while that of the platinum stem (17 mgm.) is of course relatively unimportant. As the needle was fixed to its stem by a little sealing wax, it was found essential to secure electrical contact here by a drop of starch paste (covered with paraffin wax to protect it from the drying agent). To obviate any angular play at the hook connections in the suspension, the usual device of making one of each pair of hooks out of the *flattened* end of a fine wire was adopted.

The present instrument requires a quartz fiber .006 mm. thick and 6 cm. long: this could be made thinner and only 1 cm. long or even less with advantage, for the disturbing effect of vibrations would then be lessened. The mirror is 4 mm. by 3.5 mm., and was cut from a thin galvanometer mirror.

THE SHAPE OF THE SECTORS AND NEEDLE.

It will be evident from an inspection of Fig. 1 that the smaller the angle subtended by the sectors, the less will be the sensitivity. At the same time the large gaps at the sides should not be too much encroached upon, or the needle will hardly be stable in its central position even when

[1] Most of this must be due to the projecting part of the terminal, which is not kept dry.

the small gaps are made as small as possible. It is found that sectors subtending 70° each give good results.

The shape of the needle is a matter of the greatest importance. The effect of its width and curvature, and of its distance from the sectors, upon what might be called the "angular capacity gradient" of the system for different widths of the sector gap is somewhat complex, and required a good deal of study for its elucidation. It was found that the needle can in general be stable either in the symmetrical position, or in an unsymmetrical position well to one side, and in either case the sensitivity can be adequately controlled by altering the width of the sector gap. But in the case of the unsymmetrical position the suspension must have a permanent twist, and this gives a troublesome "drift" of the needle due to its slow loss of charge; so that attempts to use this were abandoned.

In Fig. 3 are shown curves for the behavior of the needle in its sym-

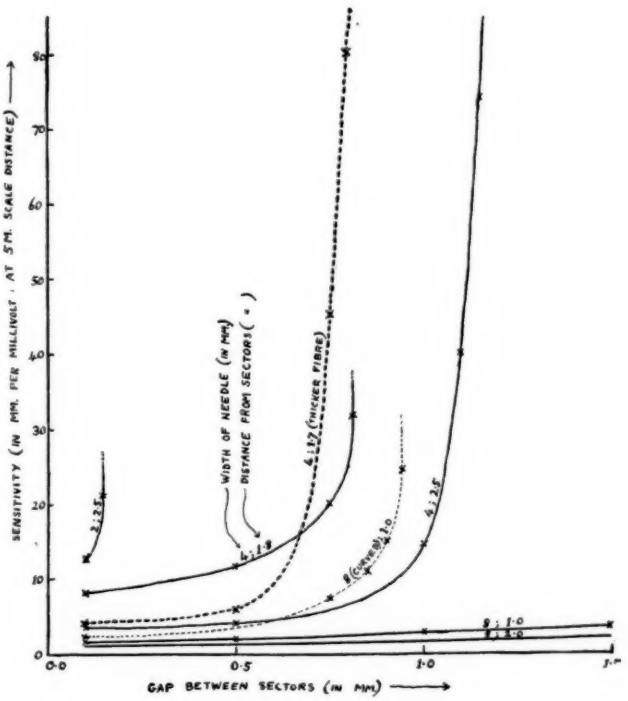

Fig. 3.

metrical stable position (the quartz fiber used being .004 mm. thick): the first number written over each curve gives the width of the needle in millimeters, and the second its distance from the sectors. It may be seen that the sensitivity increases as the needle becomes narrower and as it is brought closer to the sectors. The best needle is obviously

flat and about 4 mm. wide: the ratio of the width to length is thus about 1 : 4, and this would no doubt be best for an instrument of any size. It is not so easy to decide upon the best distance from the sectors. With any given suspension, the sensitivity increases as the needle comes closer, and also the period of swing is diminished, but instability arrives more suddenly as the sector gap widens. As, however, the use of a thicker fiber conduces to stability, the best result is obtained by using a relatively thick fiber (.006 mm.) and lessening the distance from the sectors. This plan, which combines the shorter period of swing got at the smaller distance with the flexibility got at the greater, gives the curve shown by the thick dotted line in the figure. (The thin dotted line is for a needle somewhat convex on its lower side.)

THE USE OF THE INSTRUMENT.

The torsion head is turned until the needle seems to hang symmetrically, and the latter is then charged. Now the telescope is placed at some convenient position near the window so that the scale can be seen, and the instrument roughly calibrated at this adjustment by a potentiometer. It will usually be found that the region of greatest sensitivity is not exactly at the point of zero potential, so the torsion head is turned until this state is secured, and the telescope moved again if necessary. On increasing the sensitivity by widening the sector gap, the region of greatest sensitivity remains nearly still, and any slight deviation may be corrected by repeating the above process.

Even with the symmetrical adjustment of the system there was often a slight "drift" of the needle, but the use of phosphorus pentoxide inside the case made this practically to disappear. The nature of the remaining drift and of other disturbances that occur will be seen from the following typical results. Runs over the whole scale are given at sensitivities of about 7 and about 40 mm. per millivolt, and also deflections obtained for separate 10^{-2}, 10^{-3} and 10^{-4} volt units.

It will be seen that, whereas the instrument could detect 10^{-6} volt (at a 150 *mm/mv* sensitivity) if it were steady enough, it cannot in practice detect less than about 3×10^{-5} volt, and, with the very efficient optical system used, it does this as well at a sensitivity as low as 7 *mm/mv* as at a higher. If the scale were only 1.5 meters distant, however, it would be best to use a sensitivity corresponding to about 30 *mm/mv* at the 5 meters' distance.

The cause of the unsteadiness is found to lie in an incomplete electrical shielding of the instrument; for, if the sectors are all connected to the case which is then insulated, and the whole is charged to 80 volts, a deflection corresponding to one or two millivolts is obtained. Thus

P. D. in Volts.	Scale Reading in mm.	mm./mv.
.00	573.0	
.05	886.0	
.04	831.0	5.70
.03	772.5	5.85
.02	710.5	6.20
.01	645.0	6.55
.00	575.5	6.95
−.01	505.0	7.05
−.02	439.0	6.80
−.03	378.0	6.10
−.04	320.5	5.75
−.05	266.0	5.45
.00	574.5	

Needle comes to rest in 30 sec.

Detecting 10^{-2} volt.

.00	.01	Δ
577.5	642.0	64.5
578.0	642.6	64.0
577.5	642.0	64.5
578.5	642.0	63.5
579.0	642.5	63.5

Detecting 10^{-3} volt.

.000	.001	Δ
579.5	586.0	6.5
580.0	586.5	6.5
580.0	587.0	7.0
580.0	586.5	6.5

Detecting 10^{-4} volt.

.0010	.0011	Δ
588.2	588.8	between
588.1	588.8	the
588.5	589.3	averages
588.9		+.6

.0010	.0009	Δ
588.9	588.0	between
588.7	588.2	the
588.8	588.3	averages
588.7		−.6
588.8	588.2	

P. D. in Volts.	Scale Reading in mm.	mm./mv.
.000	535	
.010	196	
.008	254	27
.006	319	32
.004	385	34
.002	455	35
.000	538	41
−.002	631	46
−.004	713	41
−.006	785	37
−.008	849	32
−.010	908	29
.000	558*	

Needle comes to rest in 90 sec.

Detecting 10^{-2} volt. (90 sec.)

.00	.01	Δ
558	900	342
558	891	333
556	897	341
565*	895	330
564	894	330
581*	910	331

Detecting 10^{-3} volt. (60 sec.)

.000	.001	Δ
592	630	38
594	632	38
590	625	35
588	623	35
596*	628	32
588	626	38

Detecting 10^{-4} volt. (40 sec.)

.0010	.0011	Δ
633	636	
632	636	between
633	638	averages
638*	639	
636.5	638.5	2.75

fluctuations of only a few volts in the "earth" charge would amply account for the disturbances observed: these fluctuations are inevitable in the neighborhood of electric lighting circuits. The defective shielding is probably due to the presence of the window, since a very good shielding of every other part of the instrument does not remove it. This difficulty will be investigated further.

The instrument becomes dead-beat when the sensitivity is raised to 15 mm. per millivolt. Its period at the higher sensitivities is not nearly as great as the time given for a reading in the table (*e. g.*, 90 sec., 60 sec., etc.), for fully two-thirds of this time is occupied by the final slow "creep" of the quartz suspension. For less accurate work good readings could be got in 20–30 sec., especially since chance disturbances would then be relatively less frequent. Also at the lower sensitivities, the first swing takes only 5 of the 30 sec. required for the needle to come to rest.

THE USE OF A FLOATING NEEDLE.

Since the torsion of the suspension is not an essential factor in its operation and stability is secured electrically, it is possible to use a floating needle. This would have the advantages of making the instrument dead-beat at all times and of eliminating the final "creep" which occupies about two-thirds of the time taken for a deflection at the higher sensitivities; but the viscous resistance of the liquid makes the instrument slow in action for needles less than 5 cm. long,[1] and also the advantage of control by the quartz fiber is lost. For the last it would be necessary to substitute an up and down adjustment of one of the sectors or something equivalent. A roughly made trial instrument with no sort of adjusting mechanism, and in which the needle takes up an unsymmetrical and very insensitive position, gives steady deflections at a sensitivity of 1 mm. per millivolt. The needle is in electrical contact with the float tank, which is insulated and kept at 80 volts, and the sectors are above instead of below the needle. The float is made of a small piece of quill tubing, and is kept vertical by a weight about 5 cm. below it. The needle is kept in its central position by the attraction of a cylindrical magnet for a little piece of iron placed on the top of the floating system.

SUMMARY.

An electrometer has been designed which can be constructed to have a capacity as low as 4 or 5 cm.,[2] and in the present model has a capacity

[1] That is, with the most efficient float yet constructed.

[2] Besides this, the capacity could be halved again by omitting one end of the needle and the pair of sectors below it.

of 9 cm. It is of simple construction and operation. Its sensitivity is great enough for the detection of 10^{-6} volt, but it has not been made steady enough as yet to detect an isolated potential difference less than about 3×10^{-5} volt in practice. It is a modification of the Dolezalek electrometer which can, by means of a mechanical adjustment, be made to work in a condition approaching instability. The way in which the stability of the needle is secured makes it possible to place it on a torsionless suspension or a float, but this plan has certain drawbacks.

THE INFLUENCE OF THE METALLIC ION IN ELECTROLYTIC SOLUTIONS UPON THE POTENTIAL DIFFERENCES BETWEEN THE SOLUTIONS AND A METALLIC ELECTRODE.

BY FLORELLA K. FINNEY.

The purpose of the investigation has been to determine the influence of the metallic ion in electrolytes in water solution upon the potential difference between the solution and electrodes of various metals. The method used has been to make cells containing two equimolecular solutions having different metallic ions and separated by a gelatine membrane, with electrodes of one and the same metal in both solutions. The direction of the current produced has indicated in which solution the metal electrode has become the more electronegative by going into solution.

According to a theory proposed by Professor F. Sanford, a metal should go into electrolytic solution the more readily as the metallic ions of the electrolyte are more electropositive. Professor Sanford tested this hypothesis for equimolecular solutions of zinc sulphate and copper sulphate, using four different metals as electrodes. It was found that when both electrodes were of the same metal, the electrode in the copper sulphate solution acted like the copper and the electrode in the zinc sulphate solution acted like the zinc in an ordinary Daniell cell. The investigation described in this paper was for the purpose of testing the hypothesis for a greater number of metals and a large variety of solutions.

The method of procedure was as follows: The base of an ordinary U-tube was filled with a freshly prepared gelatine solution. After this had set, the tube was rinsed in distilled water to remove any free gelatine, and the arms were filled with the solutions to be tested. Without delay, electrodes of similar pieces of the same metal were dipped into the two solutions. The circuit was completed through a sensitive galvanometer in series with 100,000 ohms. The deflection of the galvanometer indicated the direction of the current. The U-tube was so placed in a supporting case that the observer could observe the initial deflection of the galvanometer while dipping the metals into the solutions. A deflection of one centimeter on the scale indicated a potential difference between the cell terminals of .0036 volt.

Solutions of the nitrates, chlorides and sulphates of potassium, sodium, ammonium, barium, calcium, zinc, hydrogen, copper and ferric iron were used. Added to this list were the hydroxides and bromides of potassium and sodium, the iodide of potassium and the sulphate of nickel. The concentration of every solution was one-tenth normal (allowance being made in every instance for the water of crystallization) except in the cases of the sulphates of barium and calcium. Saturated solutions of these salts were used.

Copper, zinc, silver, nickel, cadmium, tin, platinum and bismuth electrodes were used in the course of the investigation, but most of the work was done with the first four mentioned. The direction of deflection was entirely independent of which metal was used for the electrodes, and was determined entirely by the character of the electrolytes.

Before each immersion the electrodes were carefully sandpapered, then rubbed with a clean cloth, so that their surfaces were metallic, not oxidized. The dimensions of the electrodes were roughly as follows: Rods of copper 2 mm. in diameter; nickel .75 mm.; zinc, 8 mm.; tin, 7 mm.; cadmium, 6 mm.; bars of silver 2 mm. $\times$ 4 mm. The depth of immersion varied from one to five centimeters. It was observed that though the surface of the nickel electrodes was very much less than that of the other metals, the deflections were often much greater with the nickel electrodes than with the others. Apparently some of the solutions had a tendency to induce a passive condition in nickel.

Records were kept of the deflections due to some two hundred cells. In each case three or more readings were taken of the first deflection with each pair of electrodes used; then the electrodes were reversed in the solutions and three or more readings were taken with the new arrangement. In some cases the solutions were interchanged in the U-tubes, so as to eliminate any possibility of an interaction with gelatine causing the current.

The results of the investigation show that the metals can be arranged in a series in the order in which the presence of their ions in a water solution affects the solution tension of a metal when placed in the solution. Furthermore, this series is the same as the contact electromotive series. That is, if both electrodes be of the same metal, the electrode in the solution which contains the more electropositive ion has the higher solution tension and accordingly corresponds to the zinc electrode, while the electrode in the solution which contains the less electropositive ion corresponds to the copper of the ordinary Daniell cell. The order of this arrangement of the metals was determined to the satisfaction of the writer as follows: potassium, sodium, ammonium, barium calcium, zinc, nickel, hydrogen, copper and ferric iron.

There were a few irregularities in certain solutions. Thus, while metals in KBr, KOH, KCl and KNO_3 showed a higher solution tension than in the corresponding sodium solutions, the reverse was the case with K_2SO_4 and Na_2SO_4. The metals for which this was found to be true were copper, cadmium, zinc, nickel, tin and silver. The position of the NH_4 ion was always below that of the sodium ion in the series, but in the case of the K_2SO_4 solution above mentioned the potassium ion came below the NH_4 ion in the series. This seems to indicate that if the salt used was pure potassic sulphate, the potassium ion acted abnormally in this combination. The salt in question was obtained from the supply room of the Chemistry department, and was not analyzed.

The positions of the barium and calcium ions were not checked as thoroughly as the remaining members of the series.

While zinc was found to be above hydrogen in the series, the initial deflection of the galvanometer rapidly reversed. Also, if the electrodes were not sandpapered before interchanging in the solutions the current reversed when the change was made. Careful cleaning of the electrodes before exchanging them always gave the deflection in the original direction. Exposure to the air or merely rubbing with a cloth did not remove the cause of the reversal. The electrodes with which this reversal of deflection was observed were of copper, silver, nickel and zinc.

Nickel ions are placed above the hydrogen ions in the series, but in this case, as in that of zinc and hydrogen ions, the initial deflection very quickly reversed. With nickel and zinc salts the nickel ions were consistently below the zinc ions in the series, and there was no reversal of the initial deflection. The solution tension of the metals used was found to be always higher in solutions of the acids H_2SO_4, HCl, HNO_3 than in equimolecular solutions of their copper salts.

It is an interesting result that copper, nickel and hydrogen ions in sulphate and nitrate solutions cause the electrode immersed in them to have a higher solution tension than in corresponding solutions of ferric sulphate and ferric nitrate, though iron is usually placed above these elements in the contact electromotive series. This seems to indicate that the ions of ferric iron, at least, occupy the position in the electromotive series usually assigned to passive iron. The same relation between the iron and hydrogen ions was shown with ferric chloride and hydrochloric acid solutions.

It was also found that for the same metallic ion in both solutions the solution tension of the electrodes was determined by the character of the negative ion. Solutions of the chlorides and bromides of potassium and sodium and the iodide of potassium all agreed in showing that the so-

lution tension of a metal is greater in the presence of iodine ions than in the presence of bromine ions, and is greater in the presence of bromine than of chlorine ions.

To test the influence of the concentration of the solutions, cells of copper sulphate and zinc sulphate solutions were thoroughly investigated. The investigation showed that while an increase of concentration of either solution caused a decrease of the solution tension of the metal electrode, this decrease was greater in the case of copper than of zinc ions. When the zinc sulphate solution was very concentrated and the copper sulphate solution was very dilute, the galvanometer deflection was appreciably decreased, but was not reversed.

The results of the investigation seem to the writer to indicate that, in accordance with Professor Sanford's hypothesis, the solution of any of the electrolytes used decreases the specific inductive capacity of the water, but the more electropositive an ion the less it decreases the specific inductive capacity of the water.

STANFORD UNIVERSITY, CAL.,
May, 1915.

SATURATION VALUE OF THE INTENSITY OF MAGNETIZATION AND THE THEORY OF THE HYSTERESIS LOOP.

BY E. H. WILLIAMS.

RECENTLY, Weiss[1] has shown that an alloy composed of iron and cobalt combined in relative amounts given by the expression Fe_2Co gives a much higher value of the intensity of magnetization than either iron or cobalt taken alone. Furthermore, it has been shown by Mr. D. T. Yensen[2] that the magnetic properties of pure iron can be greatly improved by melting the iron in a vacuum and it was hoped that the magnetic properties of Fe_2Co could be improved by treating it in like manner. The object of the present paper was not only to make a careful study of the saturation value of the intensity of magnetization of Fe_2Co prepared under various conditions but to use the data thus obtained in a test of the theory of the hysteresis loop as developed by J. Kunz.[3]

In his paper, Kunz tests the theory with the data then available. The results show the discrepancy between theory and experiment to be very great. If all quantities involved are obtained from the same sample, the test of the theory will be more satisfactory.

PREPARATION OF SAMPLES.

Iron and cobalt were taken in the proportion indicated by the formula Fe_2Co, melted in a vacuum furnace under pressures varying from 5 mm. to 0.5 mm. Hg, allowed to cool slowly and then forged into long bars from which samples were turned. In most cases enough of the material was taken to make both an ellipsoid and a rod—the ellipsoid for the determination of the saturation value of the intensity of magnetization and the rod for the determination of the hysteresis loop. The hysteresis data were taken by Mr. D. T. Yensen on a magnetic testing apparatus similar to those used by the Bureau of Standards. Mr. Yensen has made a study of the samples from the viewpoint of the engineer. His results are to be published soon in the General Electric Review.

[1] P. Weiss, Compt. Rend., 156, p. 1970, 1913.

[2] D. T. Yensen, Bul. No. 72, Eng. Exp. Sta., Univ. of Illinois, Urbana, Ill.

[3] J. Kunz, Phys. Zeit., XIII., p. 591, 1912.

ELLIPSOIDS.

A great deal of trouble was experienced in making ellipsoids that were accurate. The form of the ellipsoids was tested by projecting an image of the ellipsoid on the figure of an ellipsoid drawn to the desired proportions. Finally the accuracy was tested by comparing the volumes obtained by calculation, using the dimensions of the ellipsoid, with those obtained by immersion in distilled water at known temperature. No ellipsoid was used where the difference in volume differed by more than 2 per cent. and most of them differed by less than 1 per cent. The ellipsoids were about 1.19 cm. in length and about .56 cm. in diameter.

The author wishes to express his thanks to P. Weiss for samples of his material which he kindly sent. This material, when received, was porous and had apparently been melted and cast at atmospheric pressure. One ellipsoid was turned from the material just as received. A second ellipsoid was turned from a portion of the material which had been forged into a small rod, after which the remainder of the sample was remelted in a vacuum furnace under a pressure of .5 mm. of Hg. It was then forged into a rod from which an ellipsoid was turned. The results obtained with these ellipsoids are included in Table I.

The field inside an ellipsoid is uniform and is given by

$$H = H_0 - NI, \qquad (1)$$

where H_0 is the external field applied, I the intensity of magnetization, H the resultant field within the ellipsoid and N a constant depending on the dimensions of the ellipsoid.

The field H_0 was produced by a large electromagnet the pole pieces of which were 3.2 cm. apart and bored to receive a glass tube 9 mm. in diameter. On this tube was wound an induction helix. The field, H_0, between the poles of the magnet was calibrated by two methods—by means of a flip coil and with a magnetic balance. The mean of the two calibrations, which differed in no case by more than one half of one per cent., was taken to plot the calibration curve. The intensity of magnetization I was obtained by suddenly removing the ellipsoid from the induction helix between the pole pieces and noting the change of flux as indicated by a ballistic galvanometer. From the constants of the apparatus the value of I could be calculated.

If, in equation (1), NI is greater than H_0, H becomes negative while H_0 and I are still positive, *i. e.*, the field within the ellipsoid is opposite in direction to the field outside. The ellipsoids used in this work were such as to produce this result, so that when a hysteresis loop was taken with one of the ellipsoids a very peculiar S-shaped form was obtained.

RESULTS FOR I_m.

The results for the saturation values of the intensity of magnetization are summarized in Table I. In this table also, values obtained by other experimenters as well as by the author are given for comparison. Annealing these samples at 900° C. and 1100° C. produced practically no change in the values of I_m. Analysis of the first two samples of Fe_2Co listed in Table I., were made, the first showing 33.36 per cent. Co and the second 33.33 per cent. Co. From these results we see that com-

TABLE I.

Values of I_m ($t = 20°$ C.)

Commercial steel (Williams)	1,751
Swedish wrought iron (Ewing)	1,690
Bessemer steel (.4 per cent. C.)	1,770
Electrolytic iron (melted under pressure of 3 mm. of Hg (Williams)	1,798
Cobalt (1.66 per cent. Fe) (Ewing)	1,310
Cobalt (pure) (Stifler)	1,421
Cobalt (melted under pressure of 1 mm. Hg (about 99 per cent. pure) (Williams)	1,504
Fe_2Co melted under pressure of 3 mm. of Hg without being forged (Williams)	1,791
Same—hand forged (Williams)	1,962
Same—forged with steam hammer (Williams)	1,977
Fe_2Co melted under pressure of 1 mm. of Hg. Forged with steam hammer (Williams)	2,050
Fe_2Co melted under pressure of 0.5 mm. of Hg. Forged with steam hammer (Williams)	2,056
Fe_2Co melted and cast at atmospheric pressure (sample received from P. Weiss) (Williams)	1,752
Same—forged as received (Williams)	1,977
Same—remelted under .5 mm. pressure and forged (Williams)	2,038

bining pure iron for which the value of I_m is 1,800, when the iron is melted in a vacuum, with cobalt for which the value of I_m is 1,500 when melted under the same conditions, we obtain an alloy for which I_m is 2,050, or 14 per cent. higher than pure iron itself. Weiss, in the paper referred to above, states that if one takes into account the difference in atomic weight, the temperature at which ferromagnetism disappears and the densities, one finds that at ordinary temperatures ferro-cobalt has a magnetization at saturation 10 per cent. higher than that of iron, so that the extra 4 per cent. is probably due to the fact that the alloy in the present case was melted in a vacuum. This conclusion is sub-

stantiated by the difference between the last two results of Table I (material received from P. Weiss). This difference is undoubtedly due to melting under greatly reduced pressure since all other conditions are as nearly equal as it was possible to make them.

Photomicrographs of the first two samples of Fe_2Co given in Table I. are shown in Figs. 1, 2, 3 and 4. Fig. 1 is of the first sample after being forged and Fig. 2 is of the same sample after being annealed at 900° C. and cooled uniformly at the rate of 30° C. per hour. Fig. 3 is of the second sample of Fe_2Co listed in Table I. after the same had been forged and Fig. 4 is the same sample after being annealed at 900° C.

HYSTERESIS THEORY.

In the article by J. Kunz referred to above, the author obtains the following expression for the energy of the hysteresis loop:

$$W = 2I_m H_c^2 \left[\frac{1}{H_c \sqrt{\frac{I_m}{I_m + I_1 + \Delta I_1}}} - \frac{1}{H_1 - \Delta H} \right]$$

$$+ I_m H_c^2 \Delta H \left[\frac{1}{H_c^2 \frac{I_m}{I_m + I_1 + \Delta I_1}} - \frac{1}{(H_1 - \Delta H)^2} \right],$$

where I_m is the saturation value of the intensity of magnetization, H_c the coercive force, I_1 the intensity of magnetization corresponding to the magnetizing field H_1, and where

$$H = H_c \left(1 - \frac{1}{\sqrt{2}} \right)$$

and

$$I_1 = I_m \left[\left(\frac{H_c}{H_1 - \Delta H} \right)^2 - \left(\frac{H_c}{H_1} \right)^2 \right].$$

According to this theory the hysteresis loss per cycle experienced when the field alternates between the values $+ H_1$ and $- H_1$, producing the intensities of magnetization $+ I_1$ and $- I_1$, can be calculated directly if one knows the values of I_m and H_c for the material concerned.

As pointed out above, the test given this theory proved very unsatisfactory and seemed to indicate that the theory was of very little practical importance.

It seemed desirable to give the theory a thorough test by the careful determination of the four quantities I_m, H_c, H_1 and I_1 with the same sample. The results for the hysteresis loss, W, calculated and the hysteresis loss, W', as measured from the hysteresis loops are given in

Tables II., III. and IV. Table II. is for a sample of Fe_2Co before being annealed; Table III. for the same sample after being annealed at 900° C.,

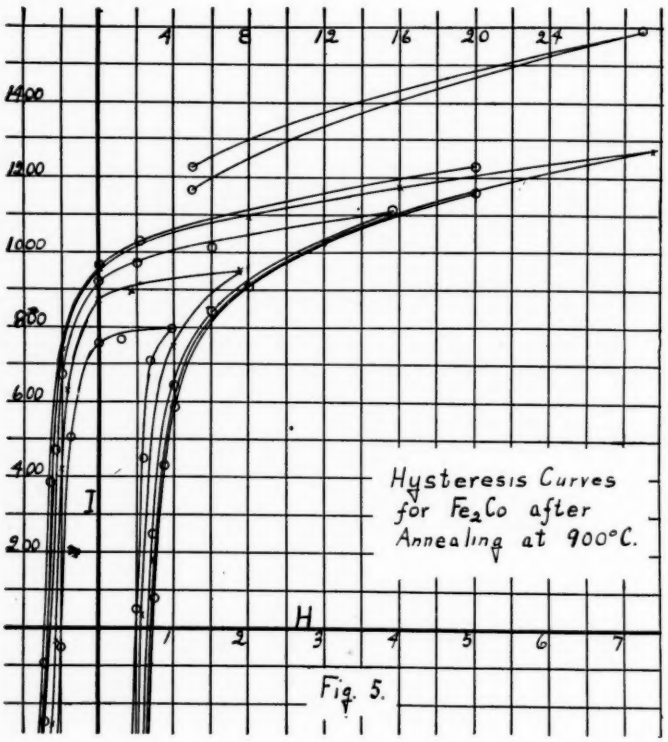

Fig. 5.

and Table IV. for a sample of pure iron after being annealed at 900° C. The hysteresis curves from which the values of W' in Table III. were measured are shown in Fig. 5.

TABLE II.

$I_m = 2{,}050$; $H_c = 6.4$; $\Delta H = 1.876$.

H_1	I_1	ΔI_1	W	W'
14	415	143.5	19,580	18,685
24.5	798	24.2	28,700	28,600
56.5	1,179	2.27	35,620	41,825
146.	1,588	.06	45,630	56,245

The results in Tables II., III. and IV. show fairly good agreement between the values for the hysteresis loss as calculated by the above formula and those obtained by measurement of the hysteresis curves.

If the theory were modified to take into account the curvature as the

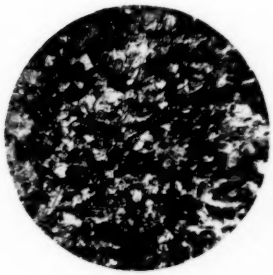

Fig. 1.

Fe_2Co melted under 3 mm. pressure and forged.

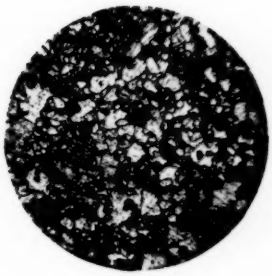

Fig. 2.

Same as Fig. 1, annealed at 900° C.

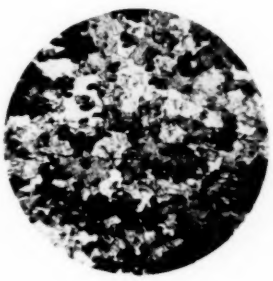

Fig. 3.

Fe_2Co melted under 1 mm. pressure and forged.

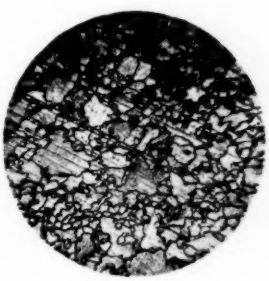

Fig. 4.

Same as Fig. 3, annealed at 900° C.

E. H. WILLIAMS.

TABLE III.

$I_m = 2{,}050$; $H_c = 0.65$; $\Delta H = 0.19$.

H_1	I_1	ΔI_1	W	W'
.95	796	537.	1,513	1,488
1.82	955	64.4	2,727	2,340
3.82	1,115	6.35	3,434	3,020
7.33	1,273	.902	3,777	3,792
29.	1,590	.013	4,166	4,930

TABLE IV.

$I_m = 1{,}800$; $H_c = 0.36$; $\Delta H = 0.105$.

H_1	I_1	ΔI_1	W	W'
.6	955	306.	973	970
0.9	1,115	81.	1,364	1,353
1.5	1,195	16.	1,651	1,552
6.5	1,264	.2	1,940	1,918

coercive force is being applied, it would probably agree with experiment even more accurately than it now does. But even as it stands the results for ordinary fields are accurate enough to make the theory of great value in calculating losses where they cannot be measured directly.

PHYSICS DEPARTMENT,
UNIVERSITY OF ILLINOIS,
May, 1915.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE SAN FRANCISCO MEETING.

THE seventy-eighth meeting of the American Physical Society was held at San Francisco, August 2 to 7, 1915. It was a joint meeting with Section B of the American Association for the Advancement of Science. The programs of the meetings on Tuesday, Wednesday and Thursday were in charge of a committee of the Pacific Coast division of the A. A. A. S., of which Professor Fernando Sanford was chairman, and those of Friday were in charge of the Physical Society, President Merritt presiding. The meeting on Wednesday was held at Stanford University, Palo Alto. All other sessions for the reading of physics papers were held at the physical laboratory of the University of California, Berkeley. General sessions of the A. A. A. S. were held in San Francisco.

The following papers were presented:

Tuesday afternoon—Spectroscopy.

(1) A Summary of the Leading Features of Electric Furnace Spectra; (2) The Spectrum of the "Tube-Arc" and a Comparison with Line Dissymmetries in Spark Spectra. ARTHUR S. KING.

Review of Laboratory Studies of the Zeeman Effect, at Mount Wilson Solar Observatory. HAROLD D. BABCOCK.

Pole Effect in the Arc and Its Relation to Other Investigations. CHARLES E. ST. JOHN AND HAROLD D. BABCOCK.

The Efficiency of Astronomical Spectrographs. JOSEPH MOORE.

Wednesday afternoon (at Stanford University).

Discussion and Demonstrations of High Potential Electric Currents. HARRIS J. RYAN.

Thursday forenoon and afternoon—Physics of the Air.

The Thunderstorm. W. J. HUMPHREYS.

New Concepts in Aërology. A. G. MCADIE.

The Application of Physical Principles to Problems Suggested by Oceanic Circulation and Temperatures. GEORGE F. MCEWEN.

Radiation and the Atmosphere. C. G. ABBOT.

Solar Radiation and Terrestrial Magnetism. L. A. BAUER.

On the Origin and Maintenance of the Earth's Negative Charge. W. F. G. SWANN.

The Natural Charges of the Elements. FERNANDO SANFORD.

Friday forenoon and afternoon.

Thermo-electric Properties of Alloys of Bismuth and Tin. A. E. CASWELL.

On the Free Vibrations of a Lecher System IV. (By title.) F. C. BLAKE AND CHARLES SHEARD.

Resistance of a Spark Gap. W. P. BOYNTON.

On the Resolving Power of Photographic Plates. ORIN TUGMAN.

Sensitive Moving-coil Galvanometers. FRANK WENNER AND ERNEST WEIBEL.

An Experimental Verification of the Law of Variation of Mass with Velocity for Cathode Rays. LLOYD T. JONES.

The Oxide Resistance Thermometer. S. L. BROWN.

New Form of Radiation Pyrometer. S. L. BROWN.

Electromotive Forces in Isothermal Metallic Circuits. GILBERT N. LEWIS.

A New Method of Determining the Amplitude of Sound Vibrations in Air—with Demonstration. E. P. LEWIS.

An Application of the Koch Registering Michophotometer for Measuring the Sharpness of Photographic Images. ORIN TUGMAN.

Photographic Study of the Tone of the Violin. D. C. MILLER.

The Variation of the Photoelectric Current with the Angle of Emission. WILLARD GARDNER.

A Quantitative Determination of the Earth's Penetrating Radiation. C. H. KUNSMAN.

Ultra-Violet Absorption Spectra. R. L. SEBASTIAN.

The Ultra-Violet Spectra of Krypton and Xenon. E. P. LEWIS.

The Law of Cohesion in Mercury. P. A. ROSS.

Note on the Theory of Ionization by Collision. W. P. ROOP.

Heat Losses from Incandescent Filaments in Air. L. W. HARTMAN.

Magnetic Field Produced by Rotating Solid Conductors in a Magnetic Field. (By abstract.) S. R. WILLIAMS.

Many physicists accepted the invitation to attend a joint meeting of Section A, the American Mathematical Society and the American Astronomical Society, Tuesday forenoon to hear addresses on "The Human Significance of Mathematics," by C. J. Keyser, Columbia University, and "The Work of a Modern Observatory," by G. E. Hale, Mt. Wilson Observatory, Pasadena. Professor Hale's address was illustrated by interesting experiments on vortex motion.

Several instructive demonstrations were arranged by Professor Lewis (some of them at the request of Dr. Hale), where they could conveniently be examined between sessions. Among them were Professor Stebbens' photoelectric cell for stellar photometry; the Zeeman effect with echelon grating, Fabry and Perot étalon, and Lummer and Gehrcke plate; mercury fringes with Fabry and Perot interferometer; the amplitude of sound vibrations made visible by the forced vibrations of lycopodium particles.

Tuesday noon visiting physicists, astronomers, mathematicians and accompanying ladies were the guests of Professors E. P. Lewis, M. W. Haskell and A. O. Leuschner, at the luncheon at the Faculty Club, University of California.

Wednesday evening, immediately after the return from Stanford University, the physicists dined together at Jules Cafe, San Francisco. Attendance about thirty.

During the week many found opportunity to visit the exhibit of the National Bureau of Standards at the Panama-Pacific International Exposition and some to make an excursion to the Lick Observatory at Mt. Hamilton, where the activities of the institution were explained by the astronomers in charge.

At the final session, a hearty vote of thanks was extended to the Pacific Coast Committee for the excellent arrangements made for the meetings, to the authorities of the University of California and of Stanford University for the accommodations provided and especially to the physics staff of the two institutions for the many courtesies extended by them.

A. D. COLE,
Secretary.